

Gas Hydrates in Energy Recovery, Transportation & Storage



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Energy Seminar, Stanford University, April 18, 07



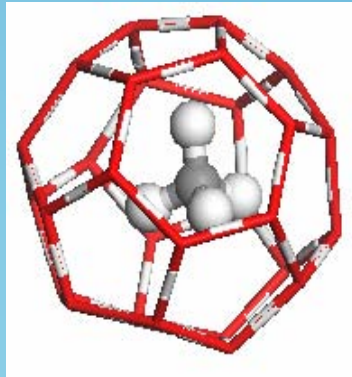
Outline

- **What are hydrates? Why are they important?**
- **Controlling hydrate formation/decomposition**
- **Highlights of CHR research**
 - Ocean Raman studies of natural seafloor hydrates
 - Hydrate decomposition for energy recovery
 - Hydrogen storage in clathrate hydrates
 - Hydrates in flow assurance
 - Molecular tools for hydrate formation/decomposition studies
- **Future directions**



What are Clathrate Hydrates? Hot Stuff!

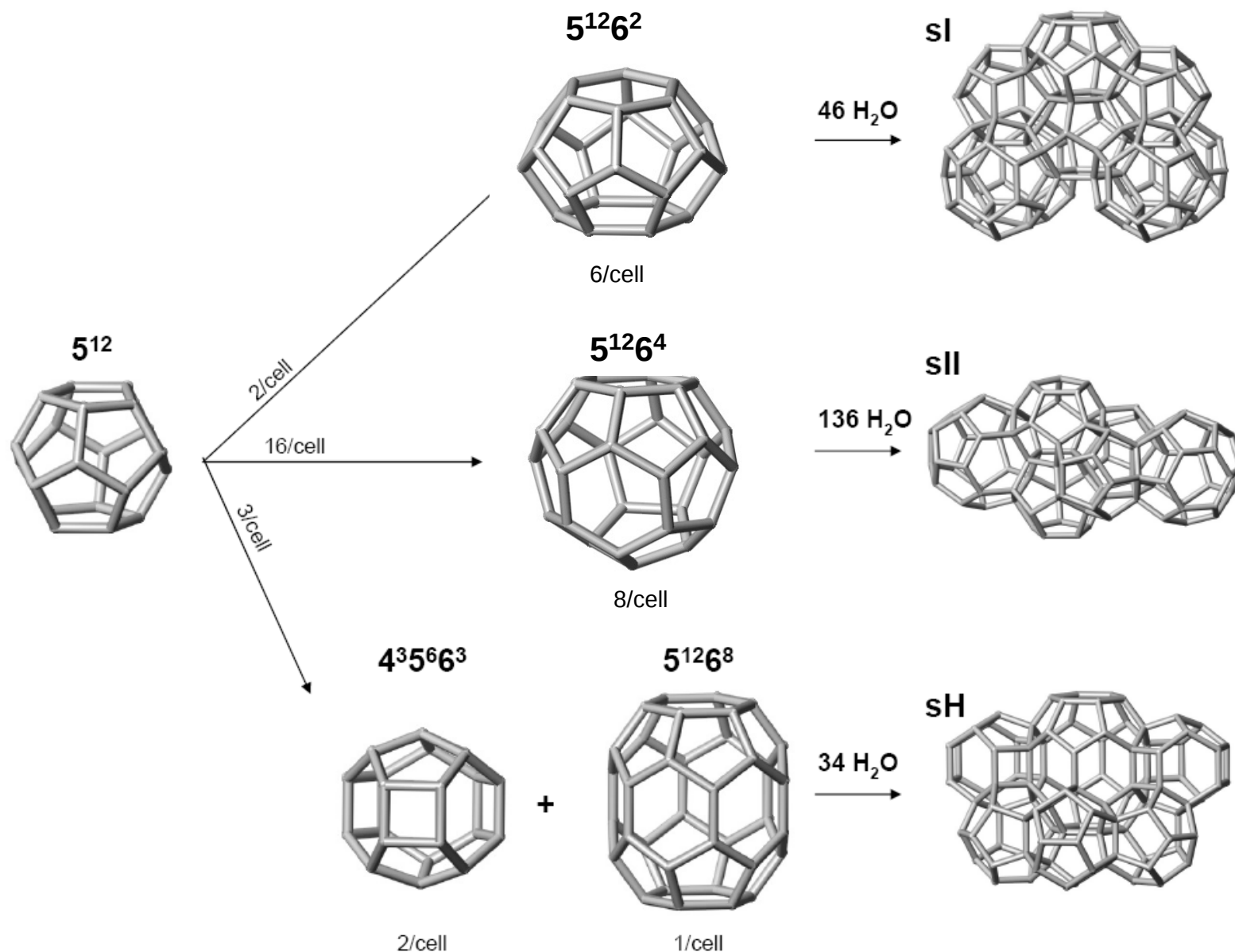
- Crystalline solids
 - Like ice
- Made of water cages
- Traps “guest” molecules
 - e.g. methane, carbon dioxide



- Concentrate large volumes of gas
 - $\sim 170 \text{ m}^3$ of gas (STP)/ m^3 hydrate



Clathrate Hydrate Structures

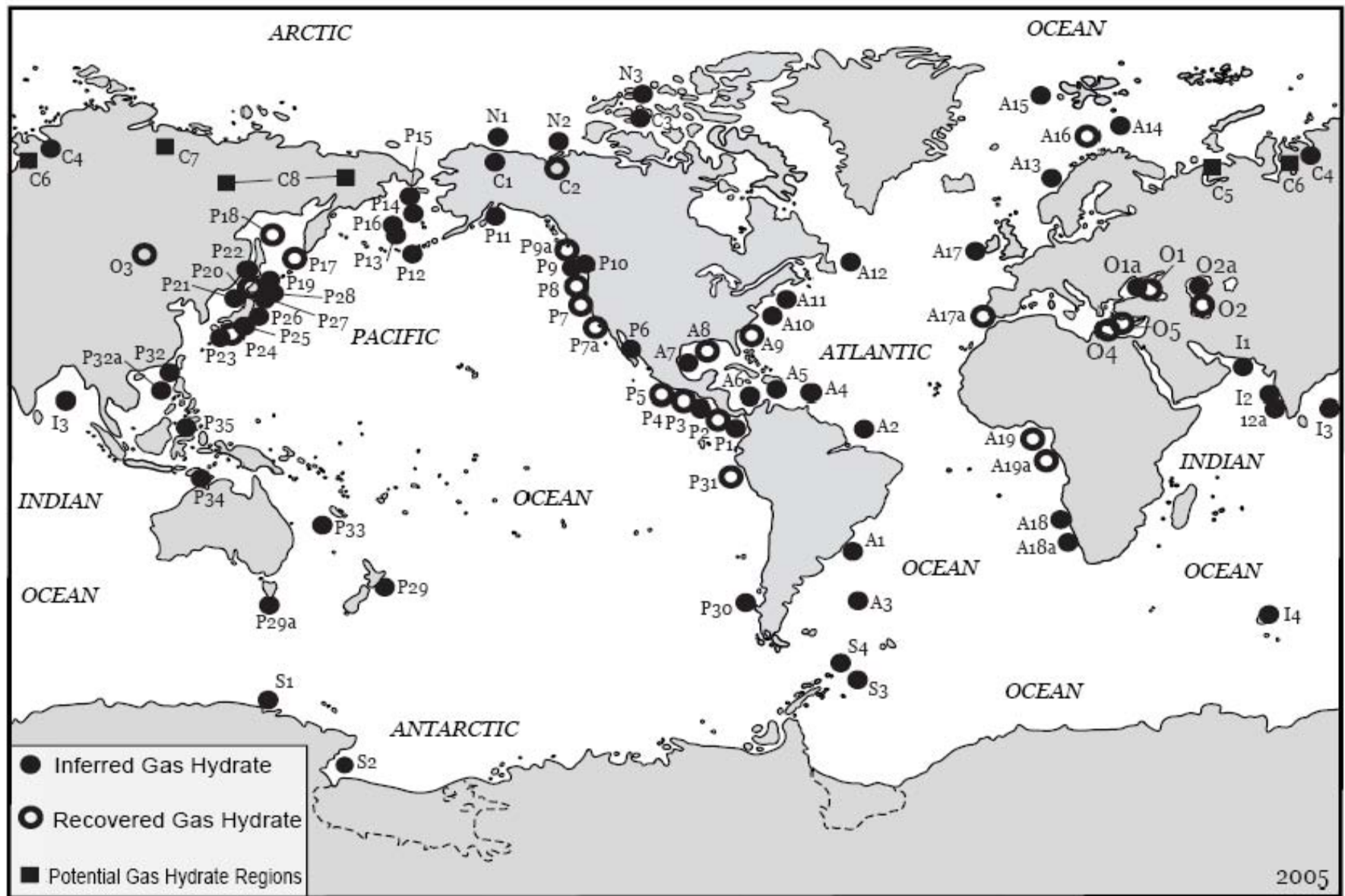


Why Are Hydrates Important?

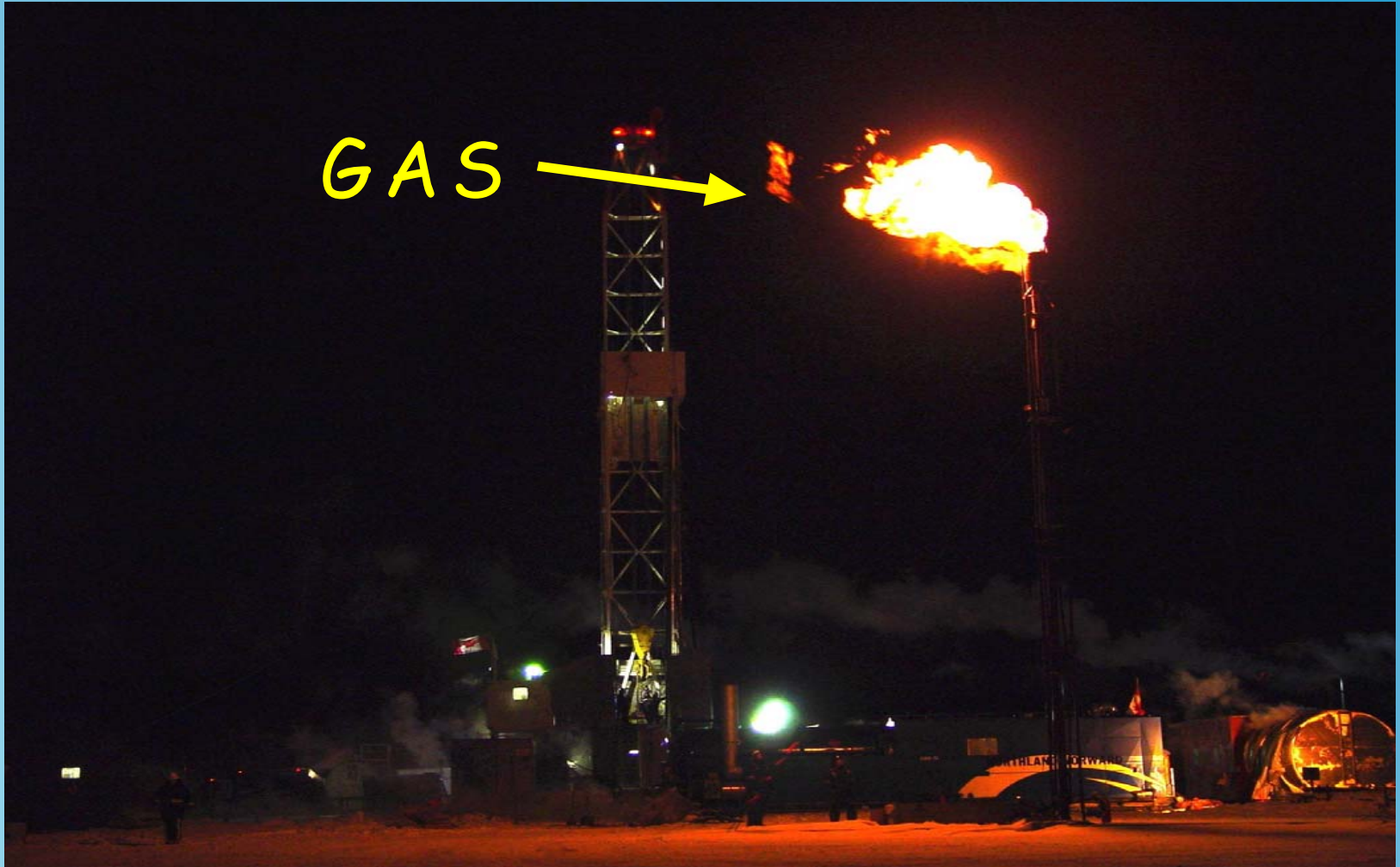


Potential Future Energy Resource

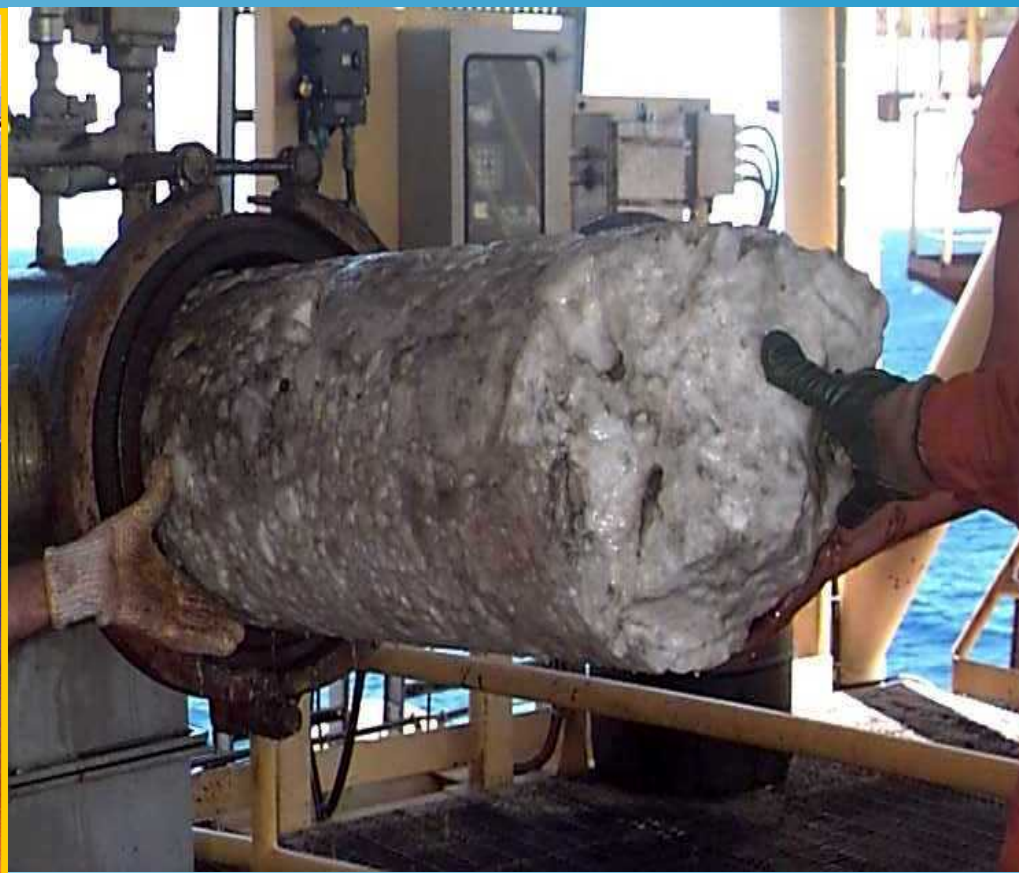
Current Estimates 10^{15} - 10^{17} m³ Hydrated Gas



Mallik2002 Gas: 468SCM in 125 hrs



Economic & Safety Risks of Hydrate Formation in Pipelines



The diagram shows a horizontal pipe with a blue fluid. On the left, a circular inlet is labeled P_{upstream} . In the center, a grey porous medium is shown. To its left, two arrows point left, labeled "friction". To its right, four arrows point right, labeled ΔP . On the right, a circular outlet is labeled $P_{\text{downstream}}$.

Hydrate Accident

[illegible]

Approach to Control Clathrate Hydrates

CSMHyK-OLGA
Multiphase Flow Model
& Flowloop Data

Sensitivity analysis
of kinetic parameters & fluids

Diffraction,
Raman, NMR
Molecular
Simulations,

Mechanisms of growth,
inhibition, decomposition

Prediction Models for Energy Recovery,
Transportation, and Storage

Hydrate
agglomeration

MMF, PSA, DSC
Rheology

Hydrate phases as a
function of time

Raman, NMR,
Diffraction, DSC,
X-ray CT, Visual



Highlights of CHR Research



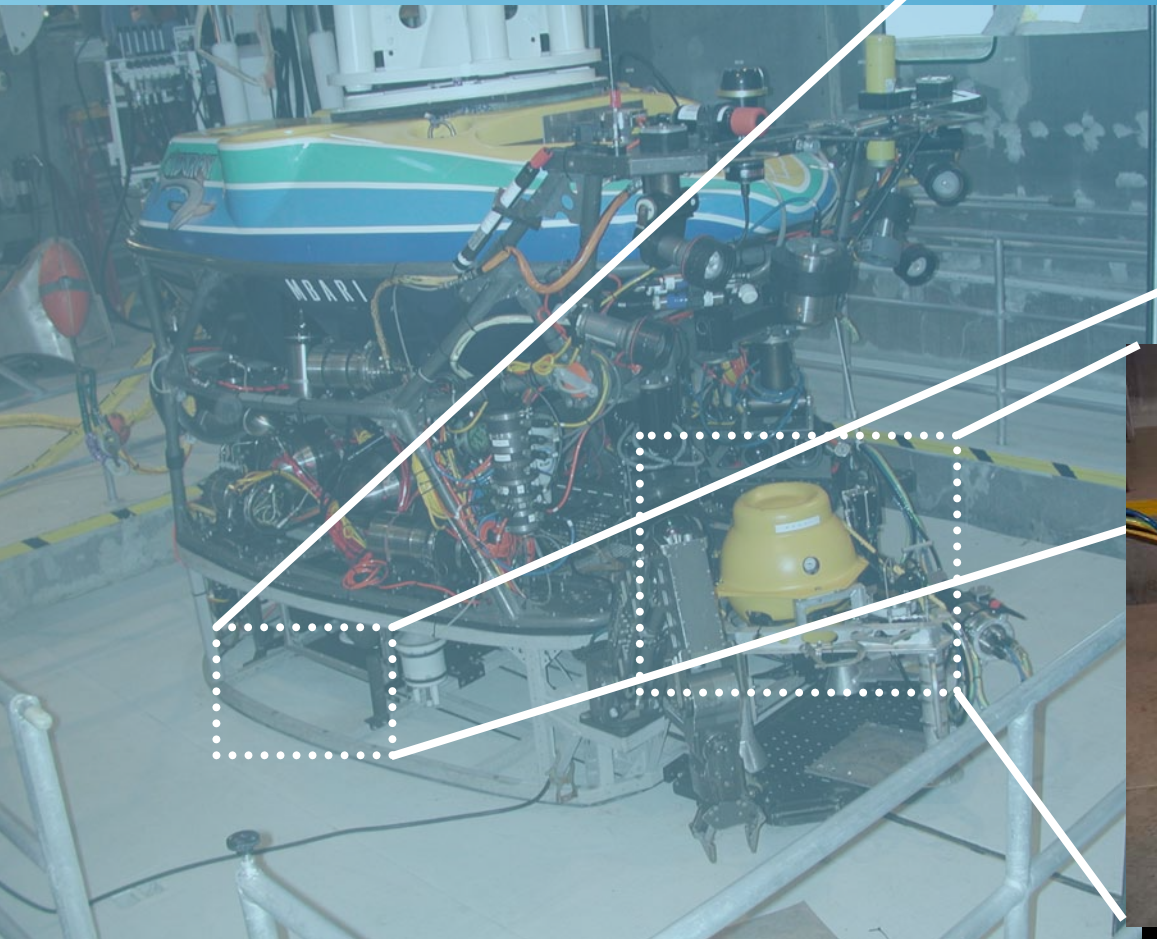
In situ ocean hydrate measurements



Ocean Raman Studies of Natural Seafloor Hydrates

Keith C. Hester (Ph.D. thesis)

MBARI ROV Tiburon



Precision
Underwater
Positioner

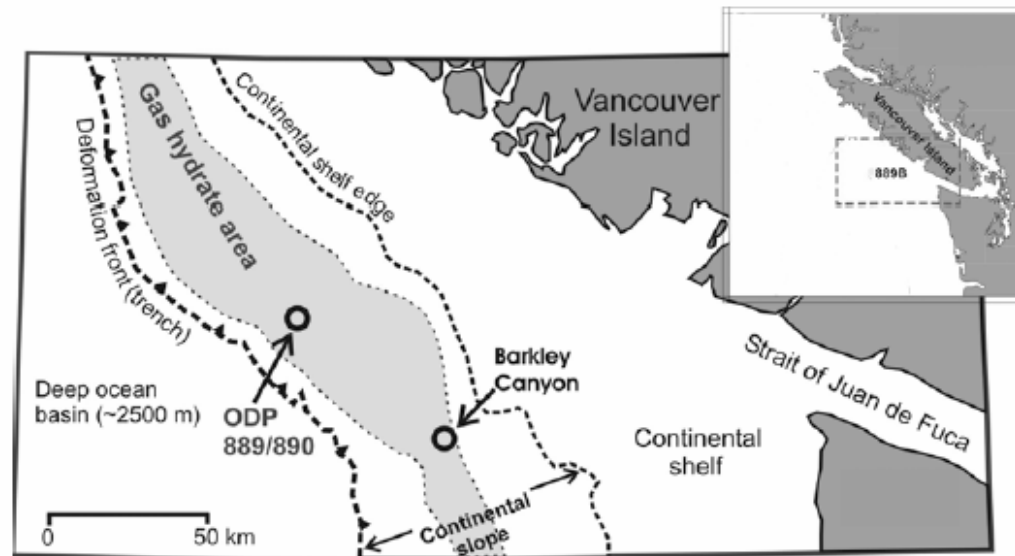


Raman probe

Barkley Canyon Expedition

August 10-19, 2006

K.C. Hester, E.D. Sloan (CSM)
P.G. Brewer, E.T. Peltzer,
P. Walz, R.M. Dunk (MBARI)



(Chapman, 2004)

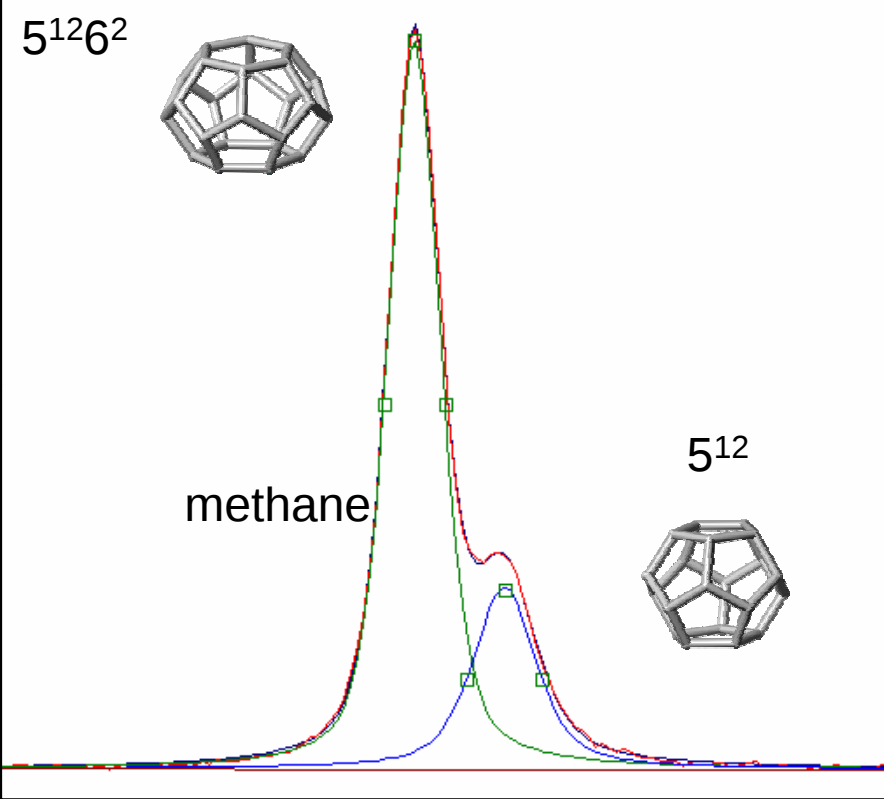
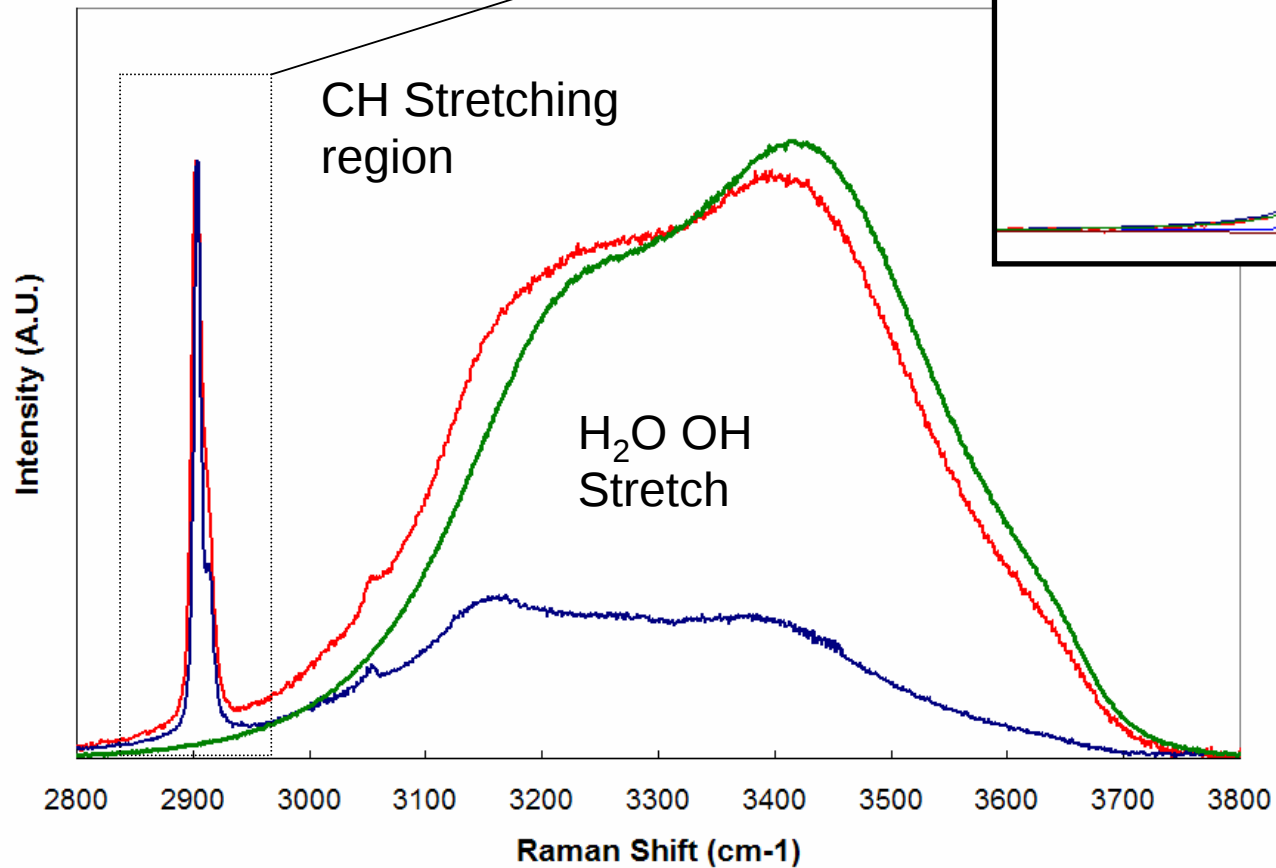
Natural hydrate mounds



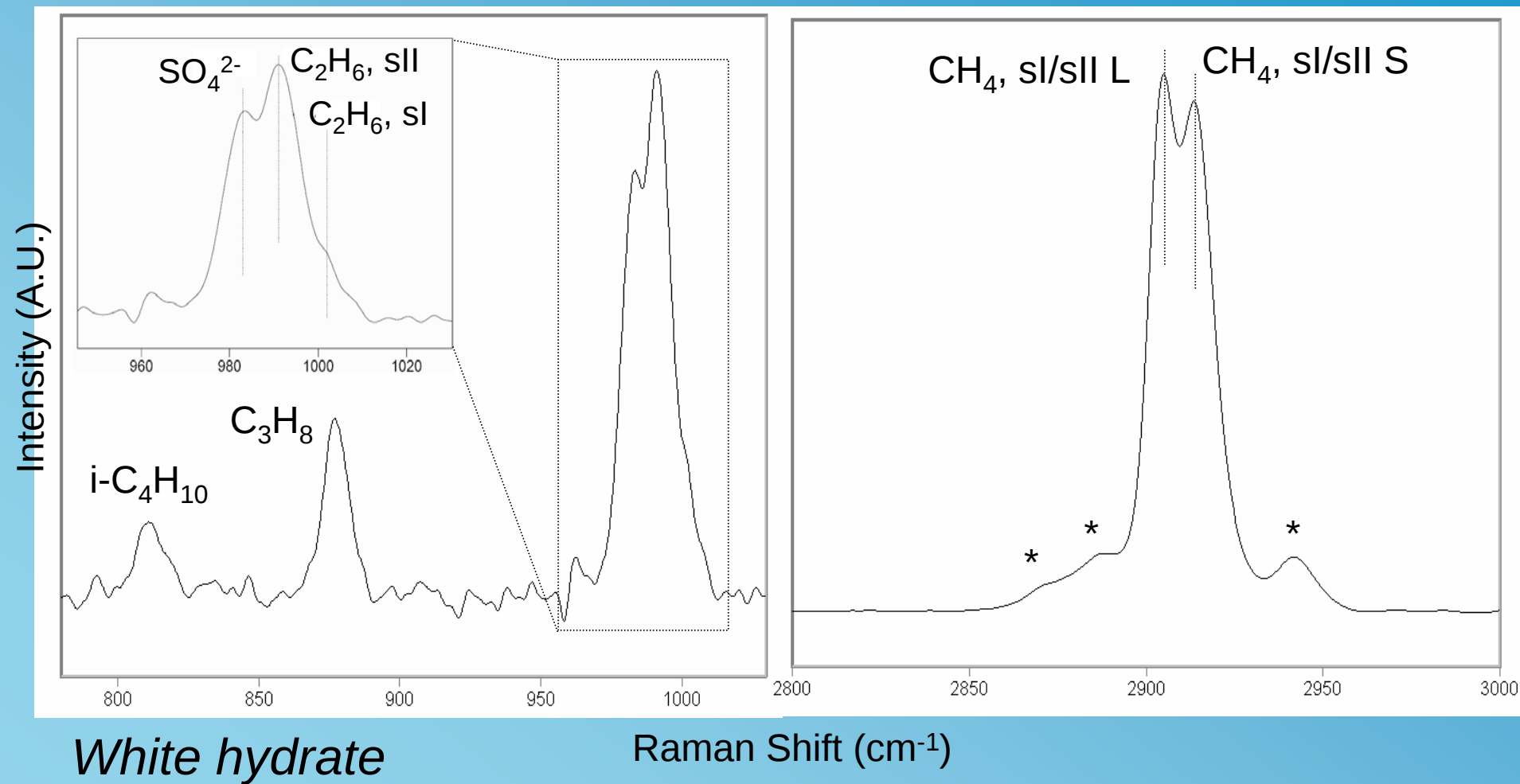
In Situ Raman Measurement



In situ Ocean Raman spectra of sl methane hydrate



Coexistence of sl/sII measured *in situ*



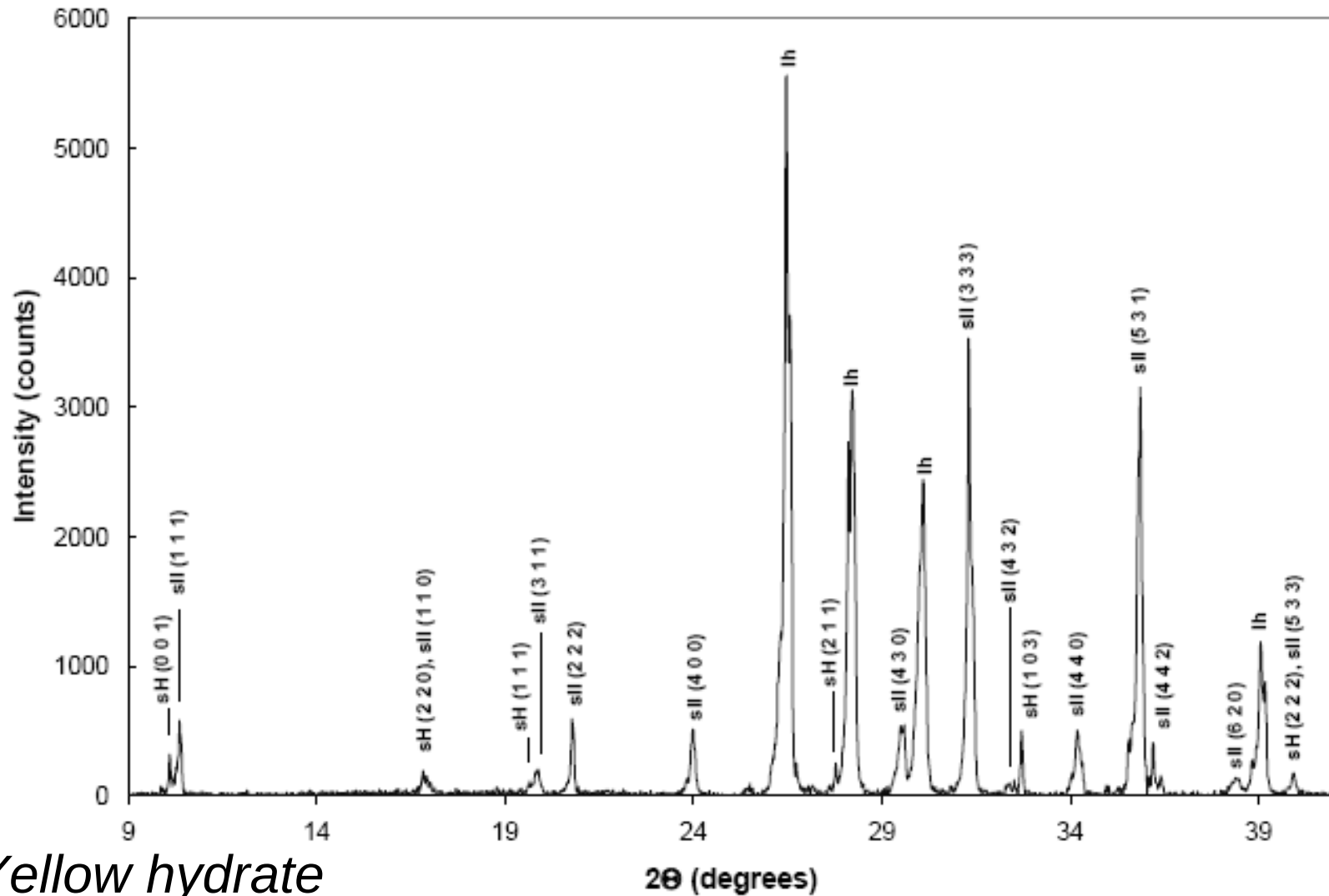
Hydrate cored recovered for laboratory measurements



- Both pressurized and non-pressurized
- Lab tools
 - Raman and NMR
 - X-ray diffraction

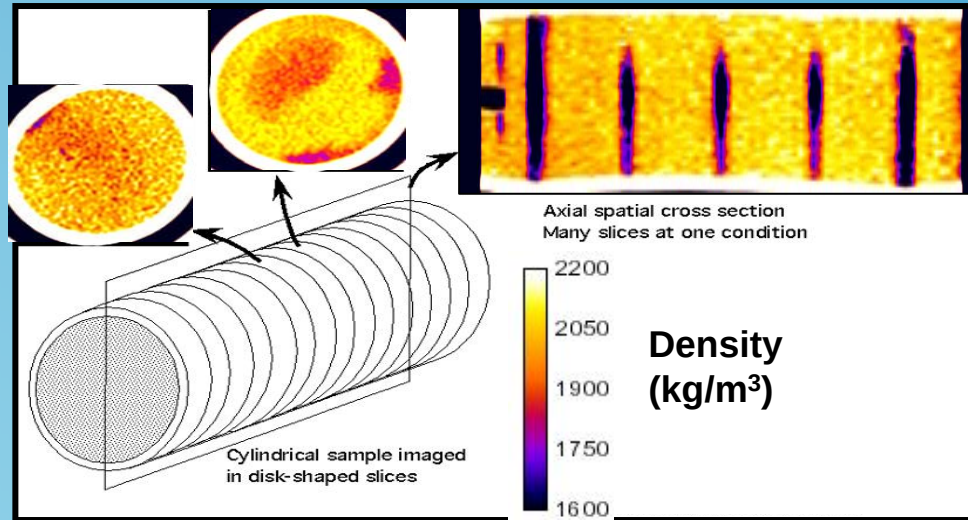


sII, sH Confirmed by XRD



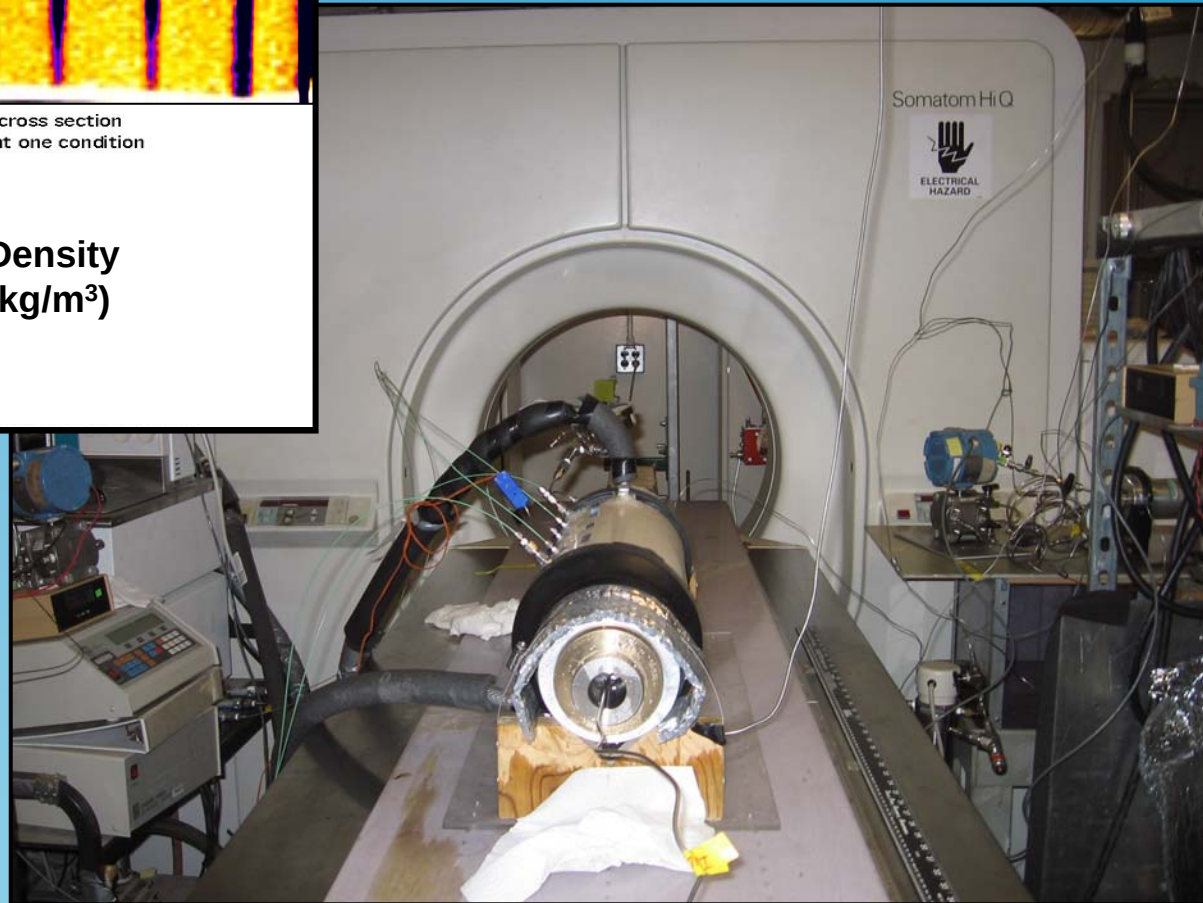
Yellow hydrate

Experiments & Simulations of Hydrate Decomposition for Energy Recovery



Arvind Gupta
(Ph.D. thesis)

**Collaboration with
LBNL**

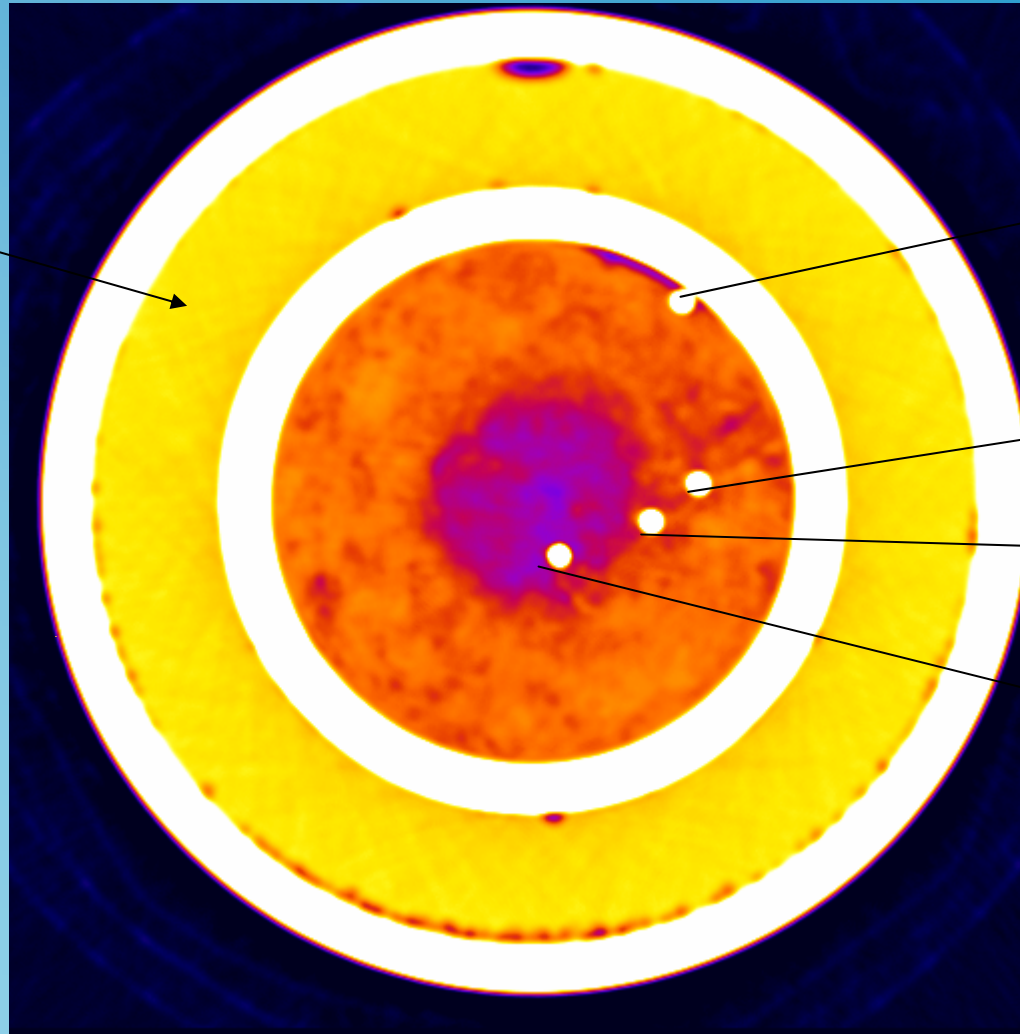




0.30 0.50 0.70 0.90 1.10 1.30
Density (g/cm³)

Hydrate Plug Decomposition Studies Using CT X-ray Measurements

Coolant



T_{edge}

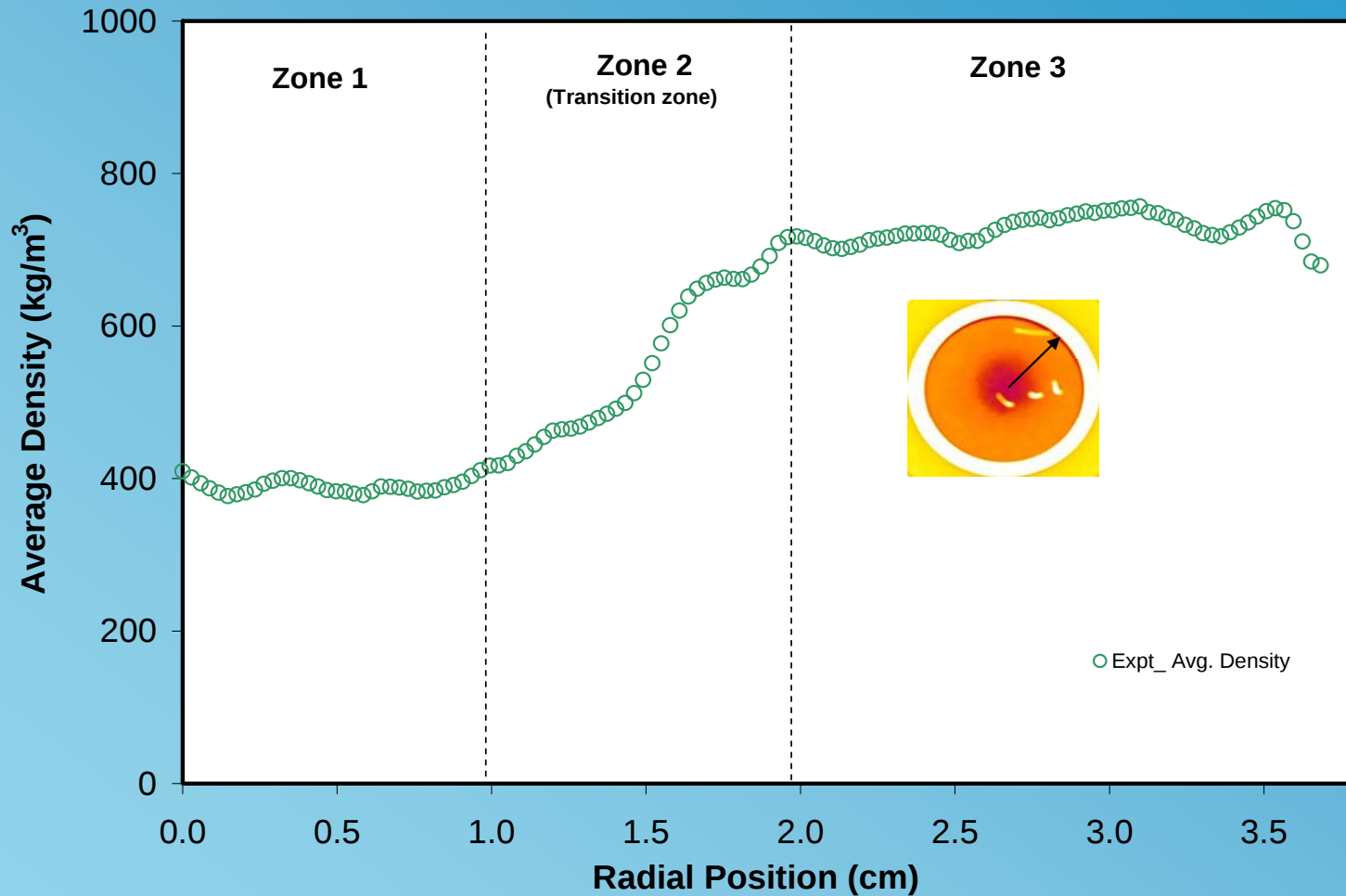
T_{outer}

T_{inner}

T_{center}

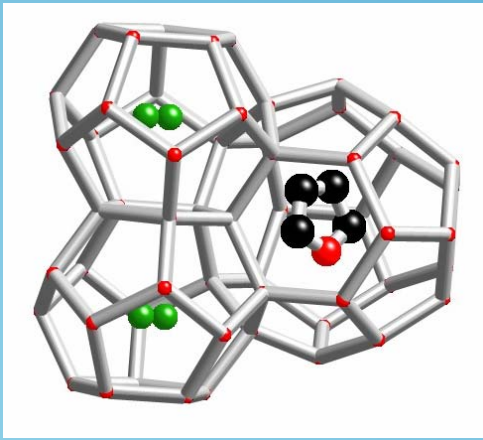


Density Profile Variation of the Hydrate Plug

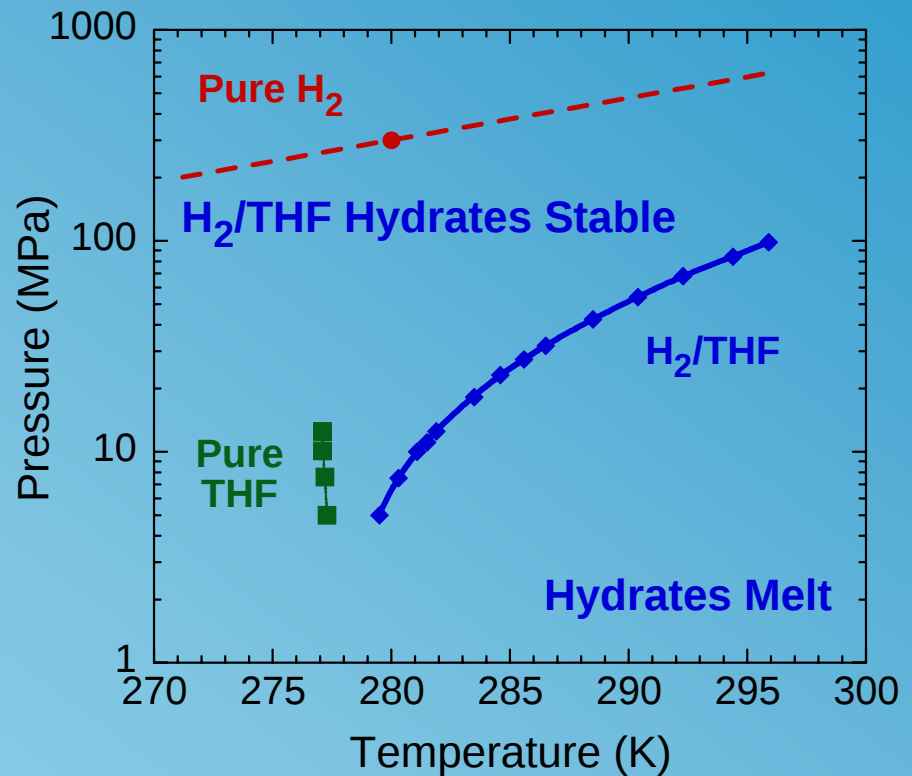


H₂ Storage in Clathrate Hydrates

- Florusse et al. Science (2004): Binary THF-H₂ hydrate (CSM & TU Delft)



Pressure reduction
2 orders of magnitude

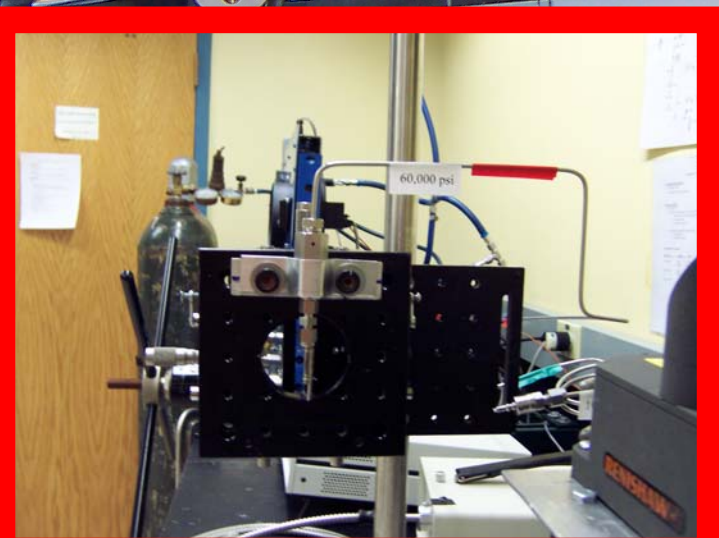
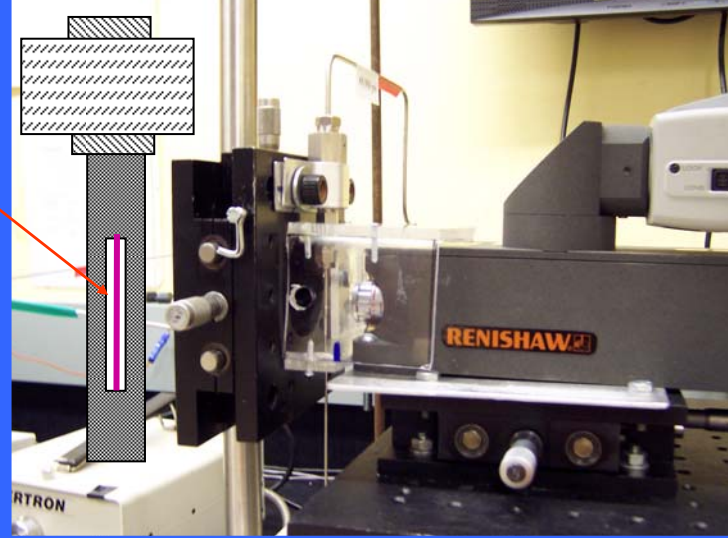




Capillary Tube
holds ~400 MPa

CAUTION:
HIGH PRESSURE
EXPERIMENT

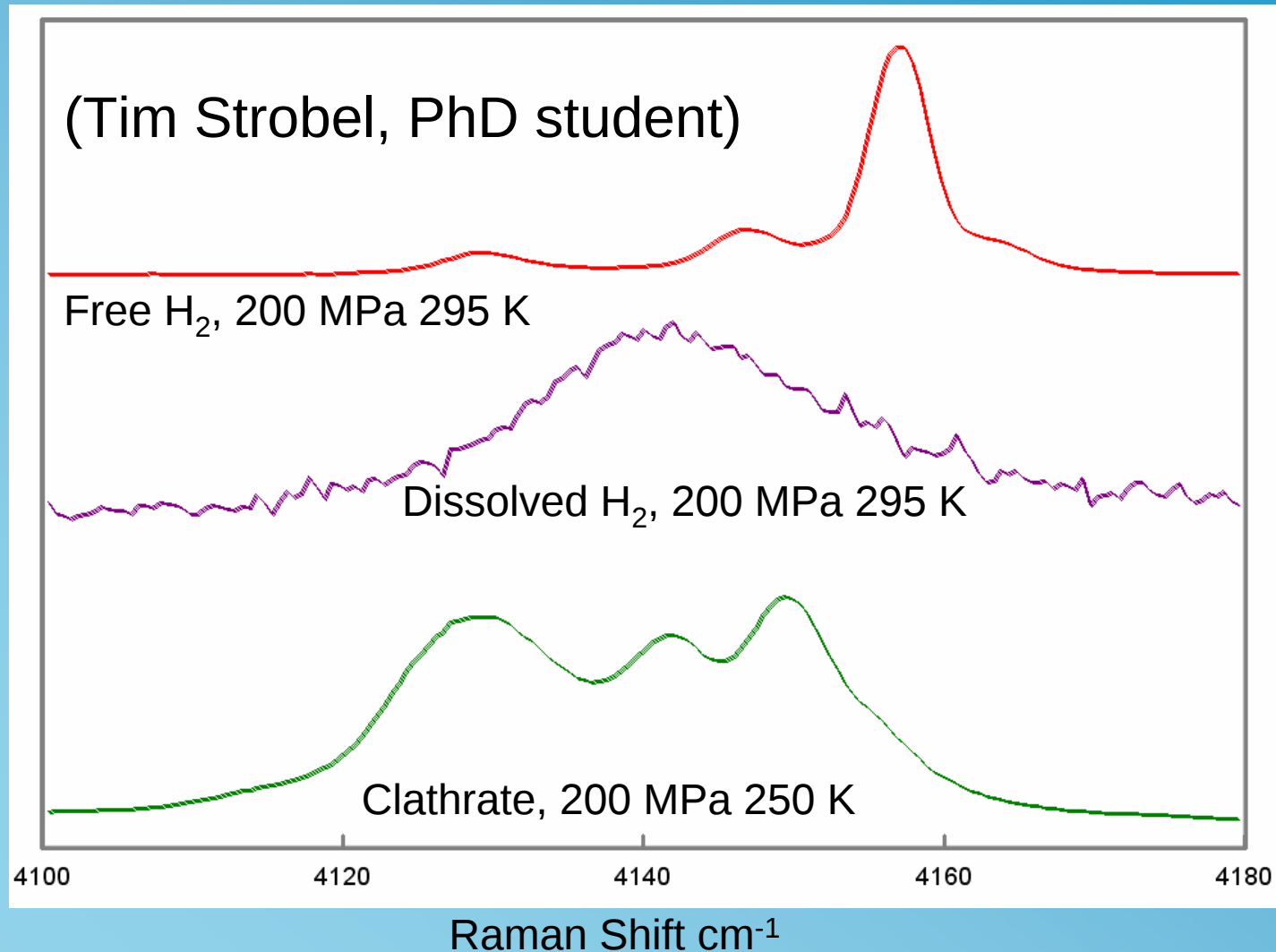
PLEASE WEAR
PROPER EYE
PROTECTION



CAUTION:
LIQUID NITROGEN

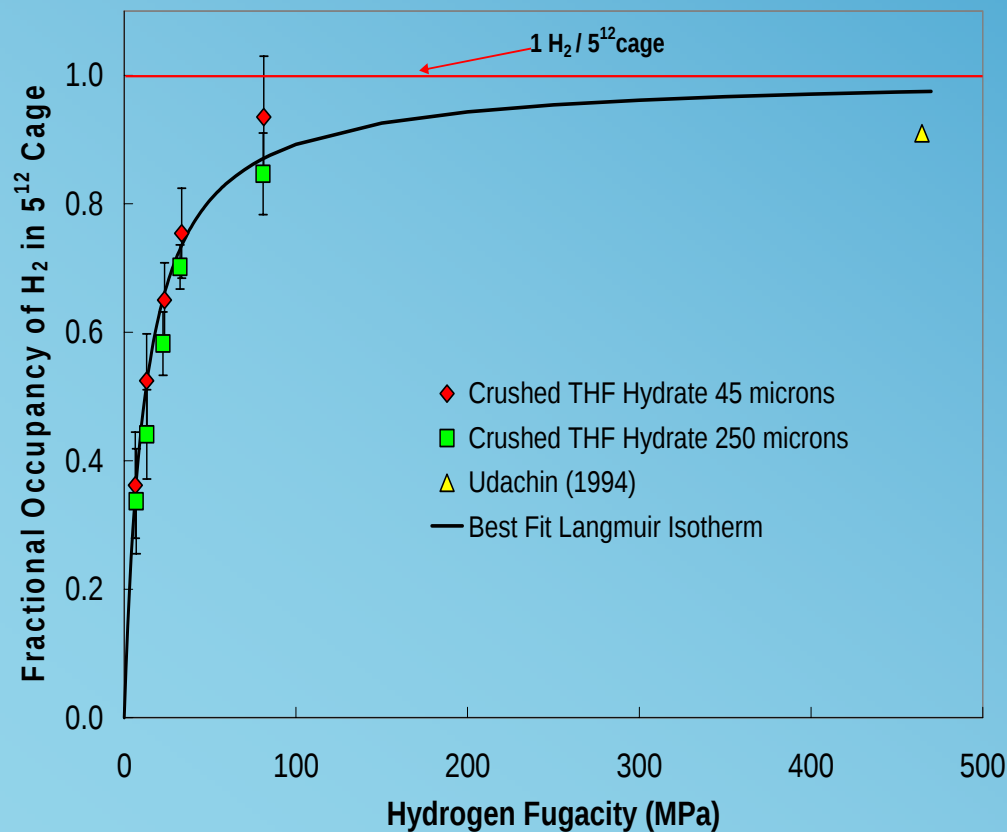
High P Raman Studies of H₂ Hydrates

Trends in H-H vibron peaks

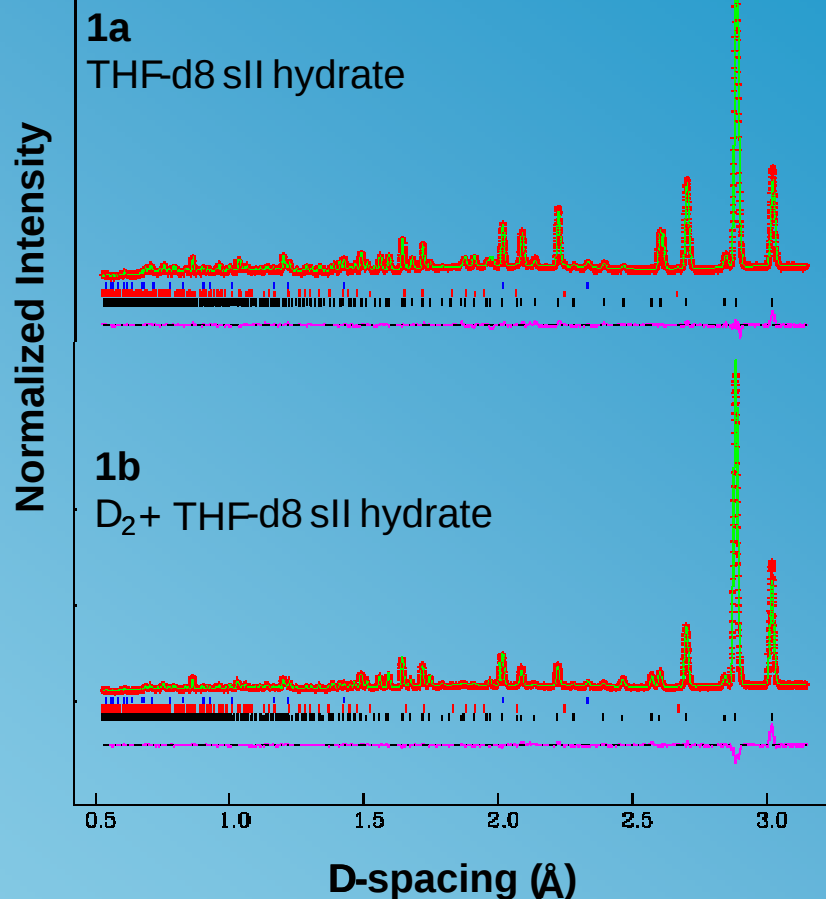


Single H₂ Occupancy Confirmed in Binary THF sII Hydrate

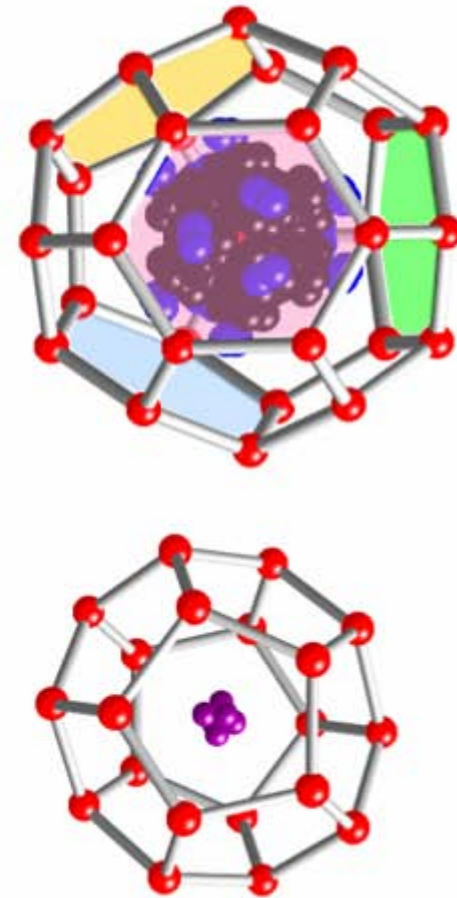
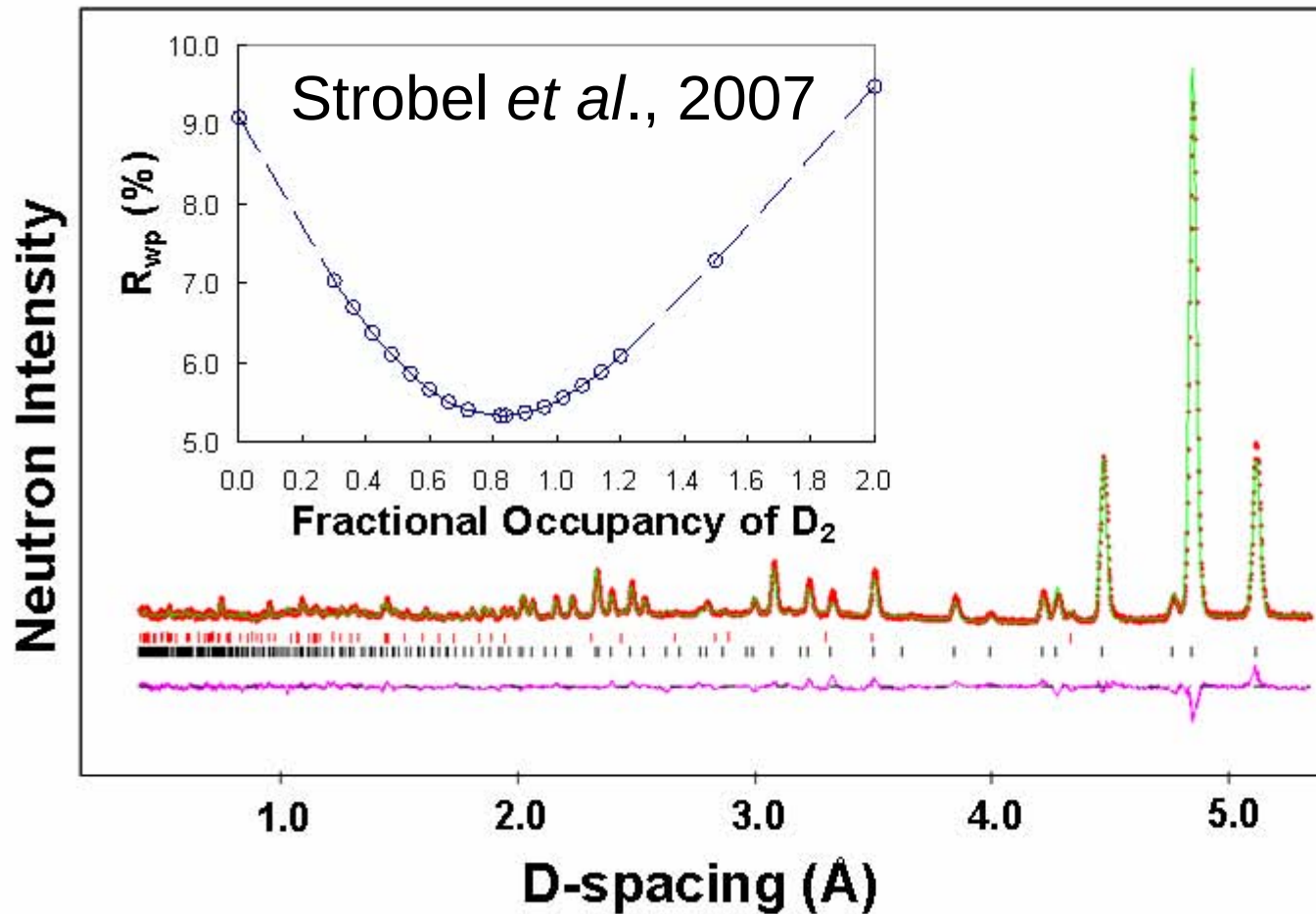
Strobel et al. J. Phys. Chem. B (2006)



Hester et al. J. Phys. Chem. (2006)

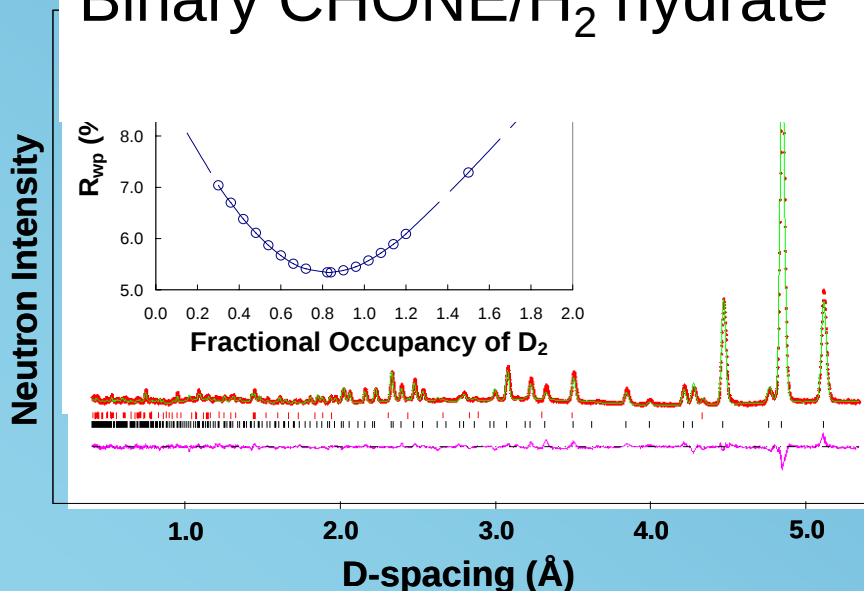


H₂ can stabilize sII binary hydrate with cyclohexanone



H₂ Occupancy in Binary & Pure H₂ Hydrates: 1 H₂ in sII 5¹² Cage & 1-4 H₂ in 5¹²6⁴ Cage

Binary CHONE/H₂ hydrate

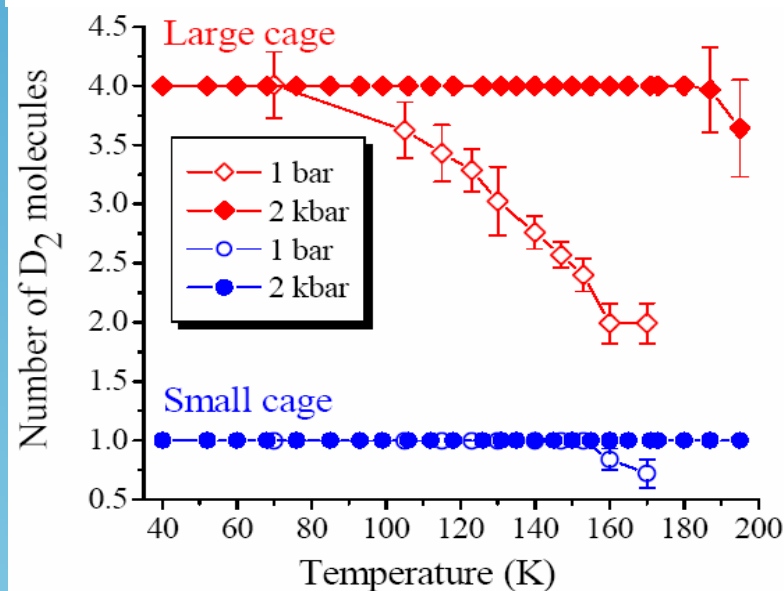


Strobel et al., 2007

Hester et al., J. Phys.Chem. B, 2006

Strobel et al., J. Phys. Chem. B, 2006

Pure H₂ hydrate



Lokshin et al., 2004



Hydrates in Flow Assurance



On the Cusp of a Hydrate Change

Avoidance

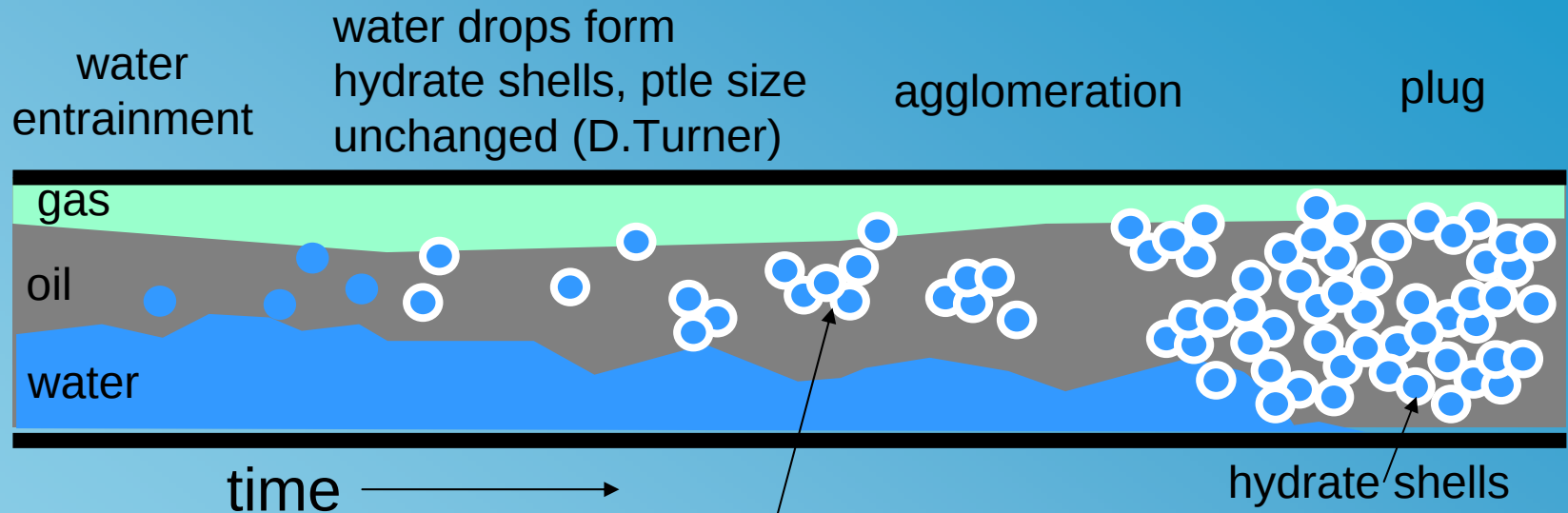
- Avoid Hydrate T&P
 - Thermodynamics
 - Time Independent
 - Within 1.4°F; 10%(P)
- Avoid T&P
 - Insulation
 - Inhibitor Injection

Management

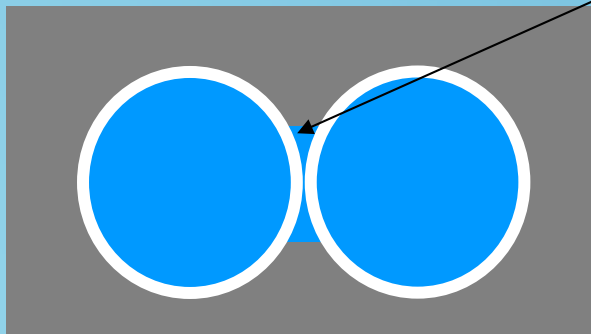
- Prevent Blockages
 - Kinetics
 - Time Dependent
 - No Agglomeration
- Examples
 - Anti-Agglomerants
 - Slurry Flow
 - Plug Remediation
 - Electrical Heating



Conceptual Model of Hydrate Formation in Oil-Dominated System

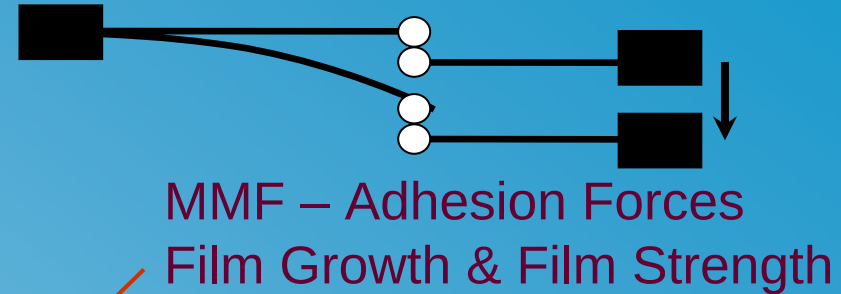
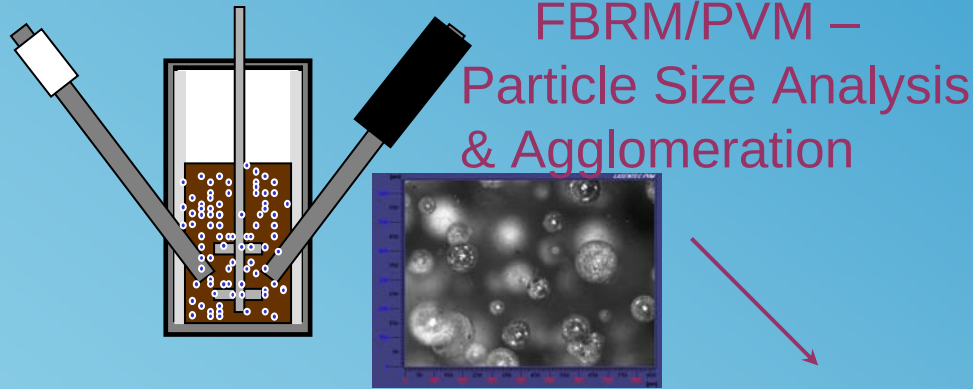


capillary attraction

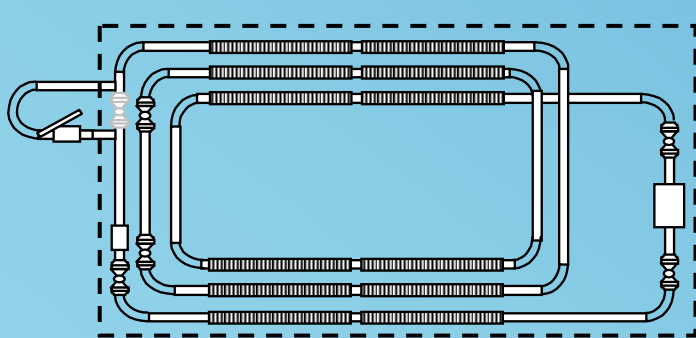


Agglomeration Prevention = Plug Prevention

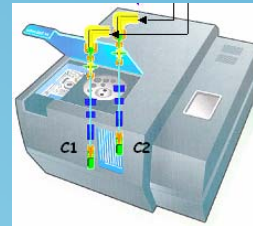
Model Development to Predict Hydrate Blockages



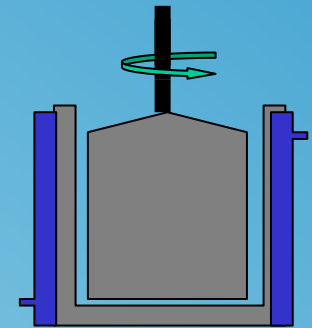
CSMHyK/OLGA 2000 Simulator
Hydrate Growth in Multiphase Pipeline Flow



Flow Loops (Texaco,
ExxonMobil, TU)



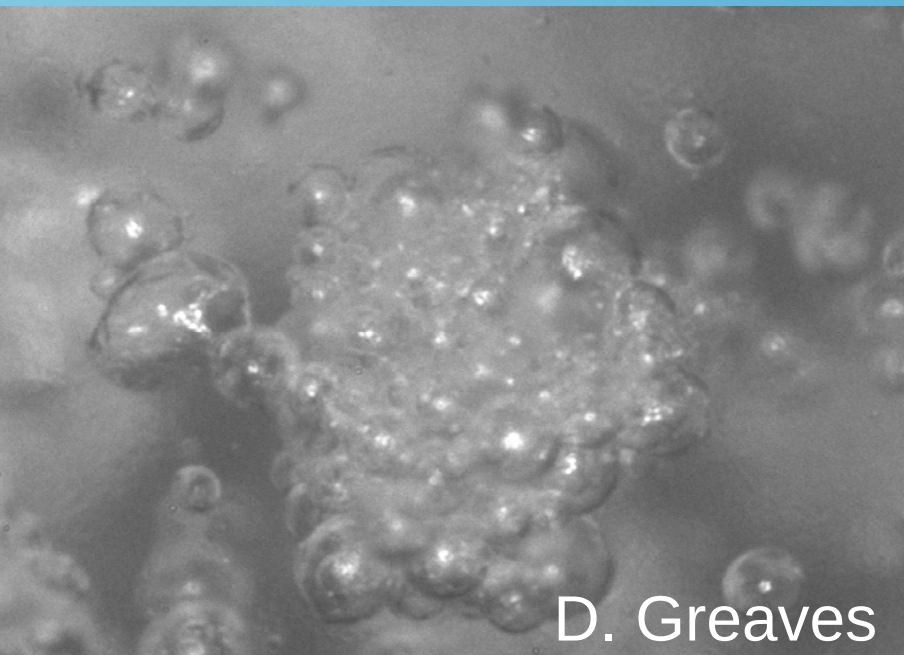
HP-DSC -
Agglomeration



Rheometers



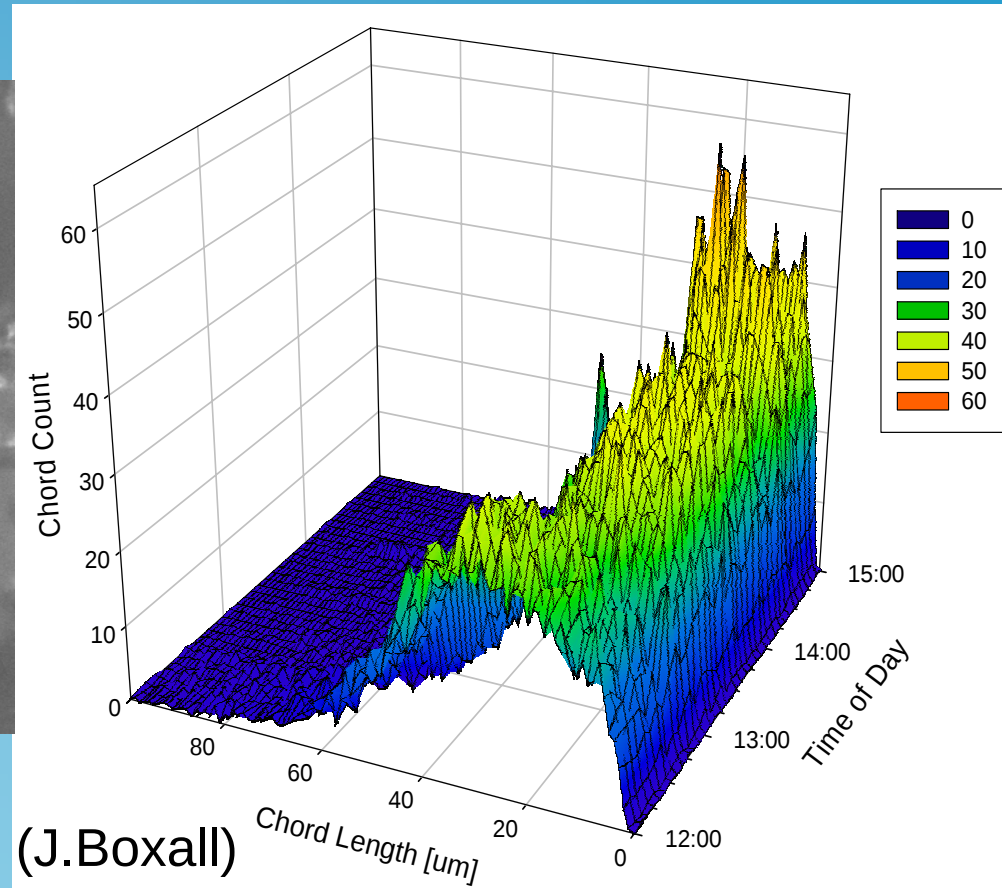
Hydrate Agglomerate Morphology Determined with Simultaneous PSD



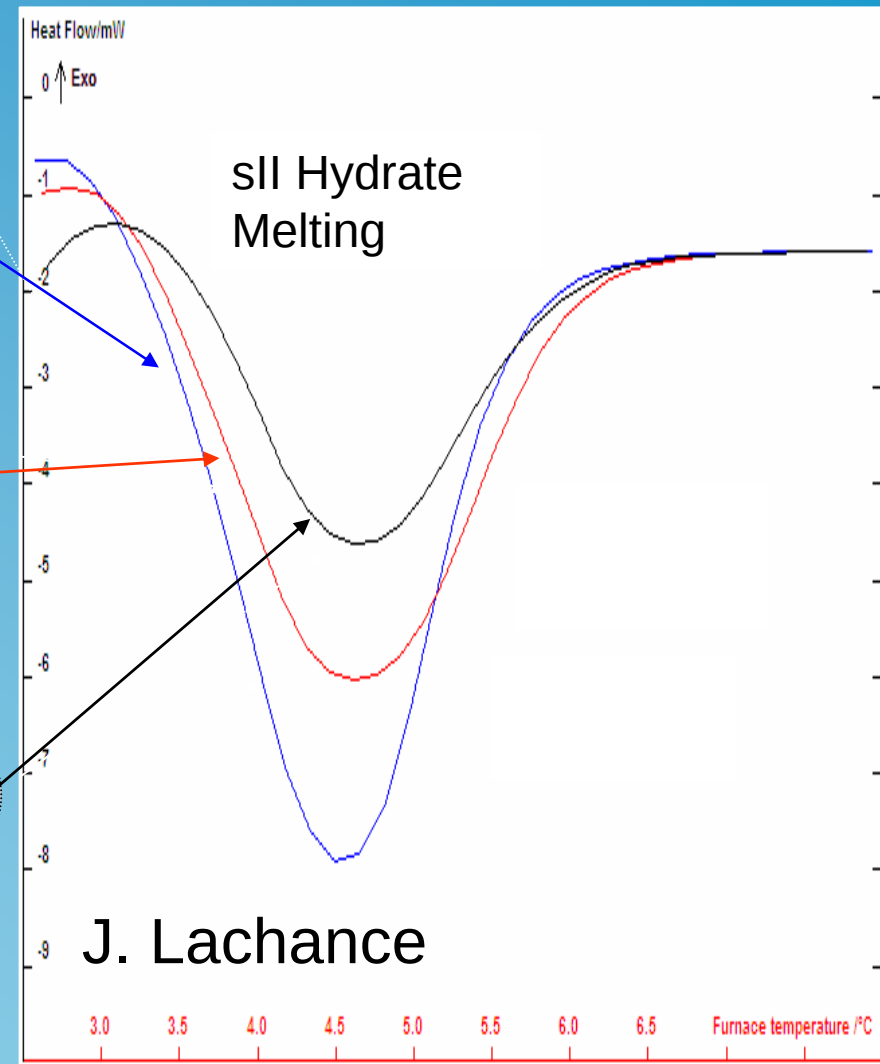
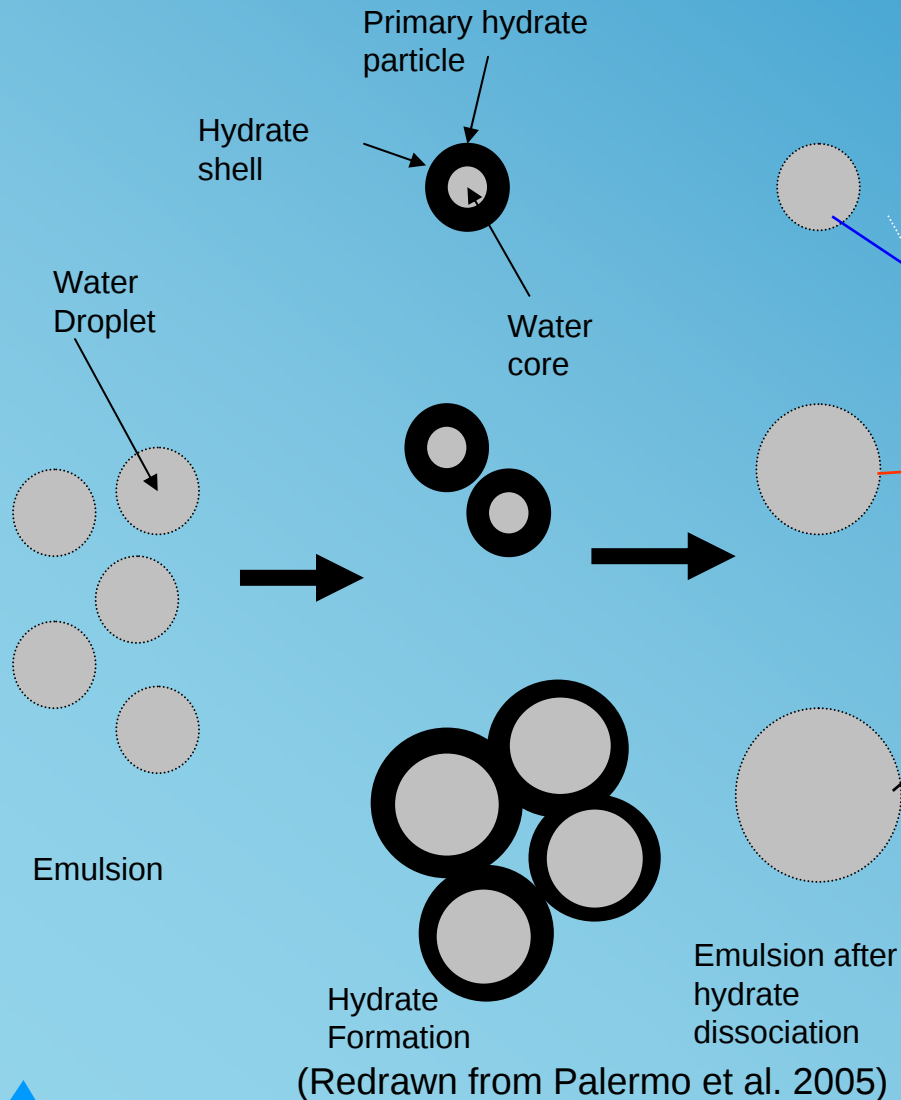
D. Greaves

PVM

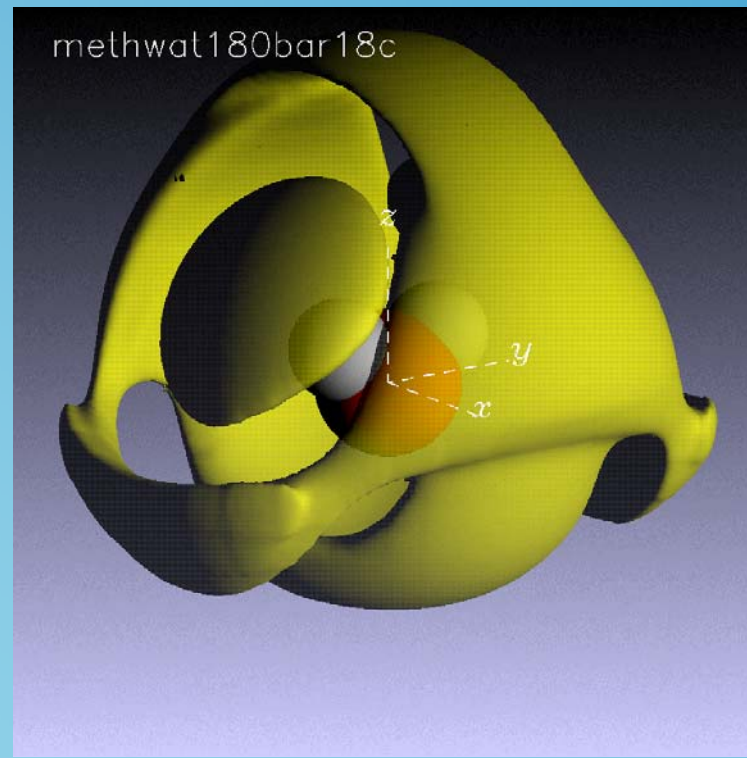
FBRM



DSC Tests of the Effect of Hydrates on Emulsion Stability



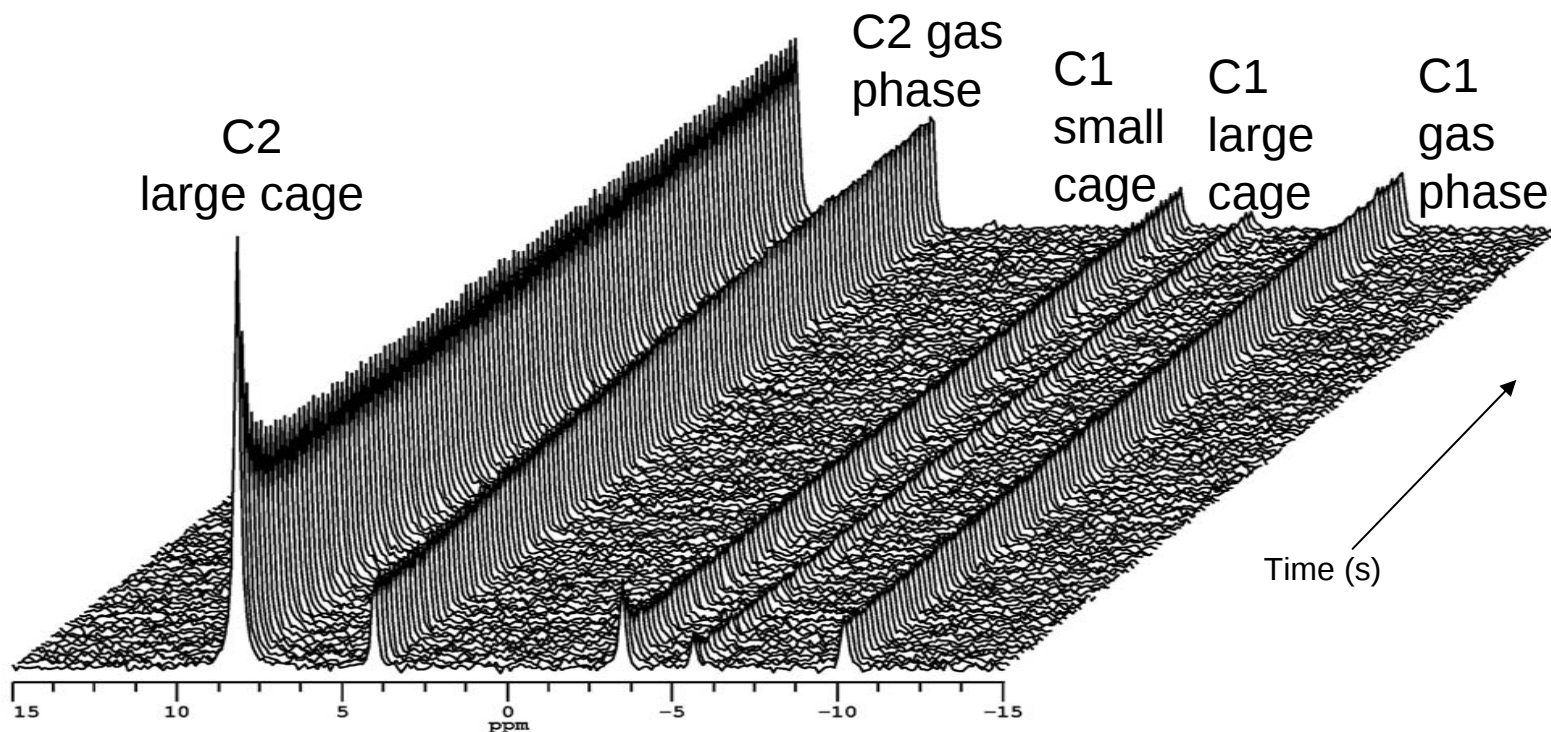
Molecular Tools to Study Hydrate Formation & Decomposition



Time-Resolved NMR

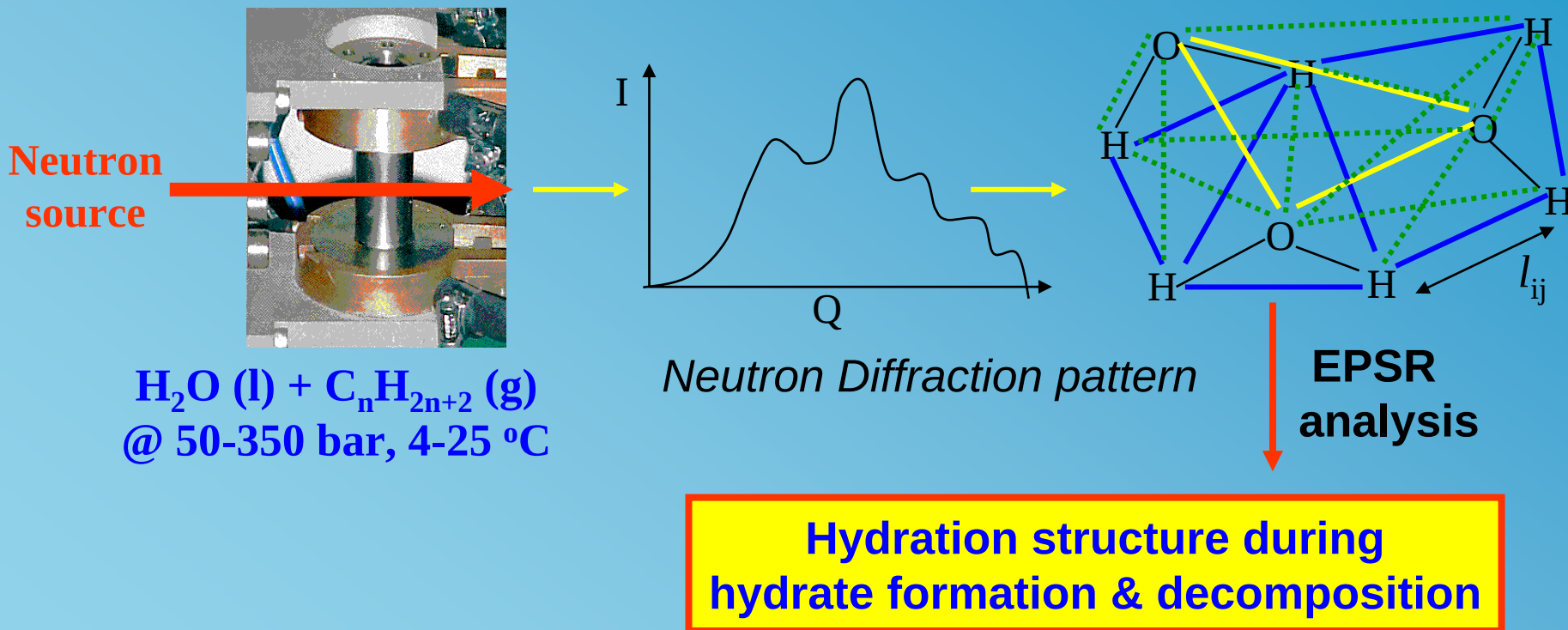
^{13}C MAS NMR of $\text{CH}_4\text{-C}_2\text{H}_6$ Hydrate

$5^{12}6^2$ cages decompose faster than 5^{12} cages



Dec et al., J. Phys. Chem. B, 2007

Molecular-level Studies of Hydrate Formation & Decomposition

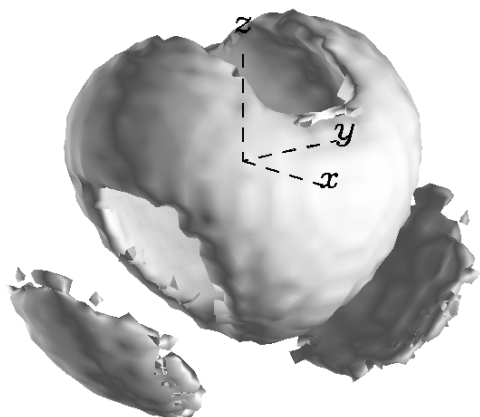


Buchanan, Soper, Koh et al., J.Chem. Phys. (2005)
Thompson, Soper, Koh et al., J. Chem. Phys. (2006)



Hydration Shell Expands on sl & sII Hydrate Formation

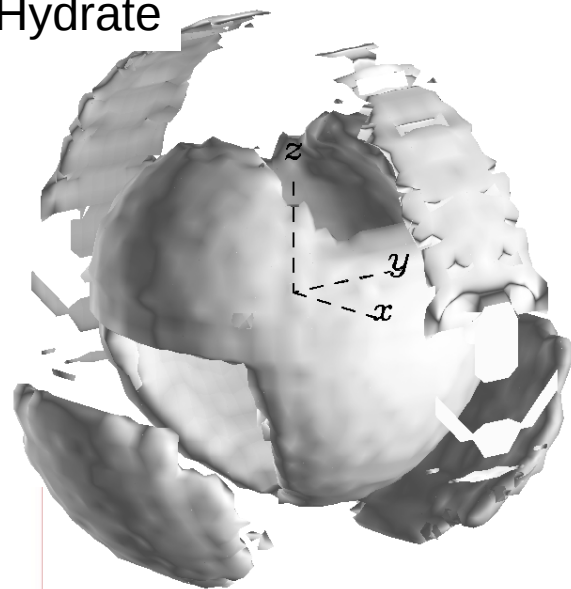
Liquid



~1-2 Å expansion

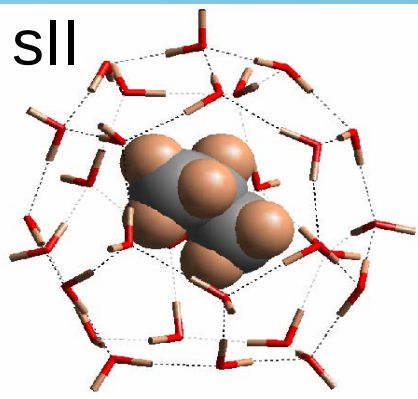


Hydrate

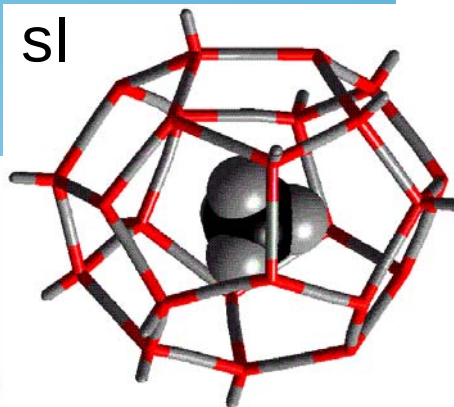


Increased order

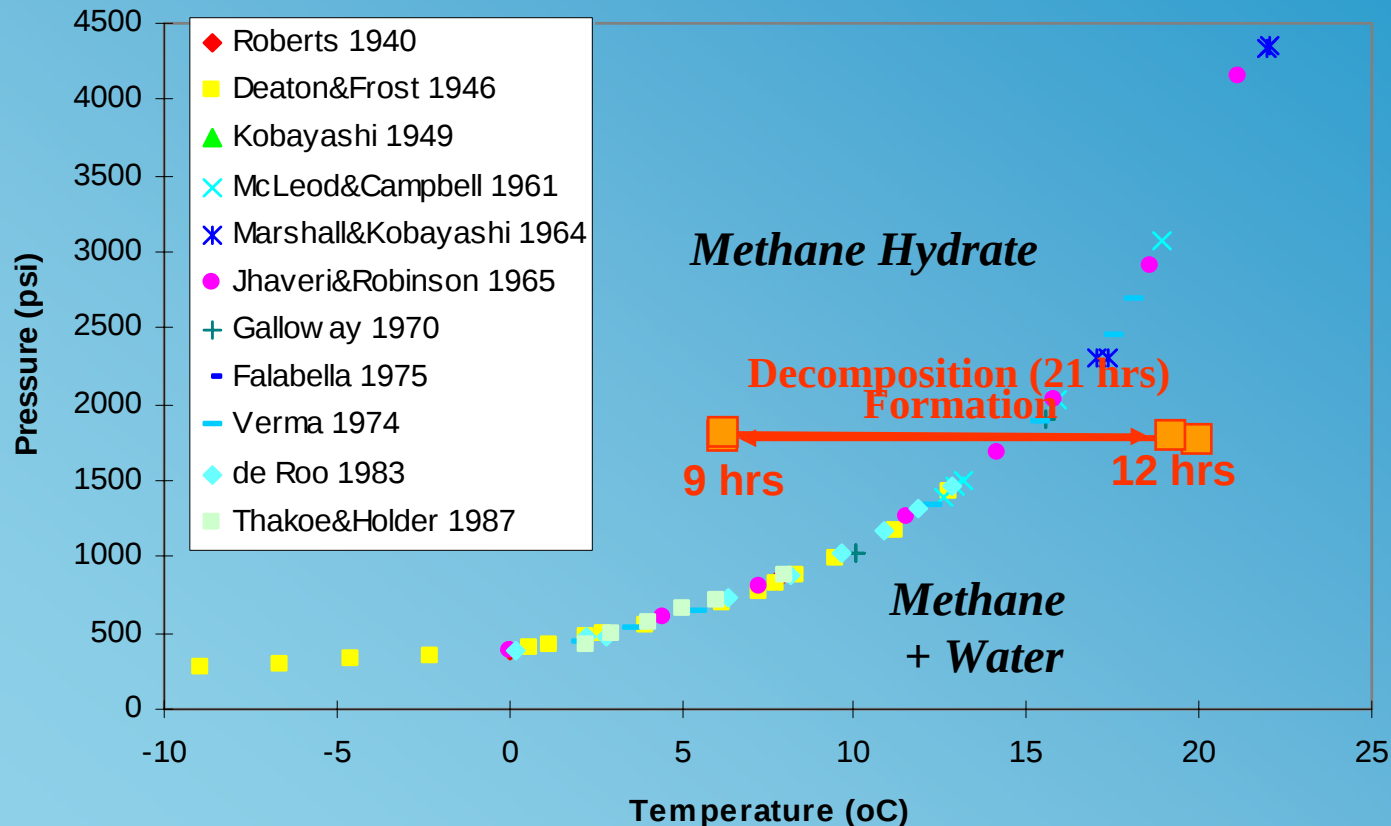
sII



sI



Hydrate Decomposition Over 21 hours To Remove Bragg Peaks

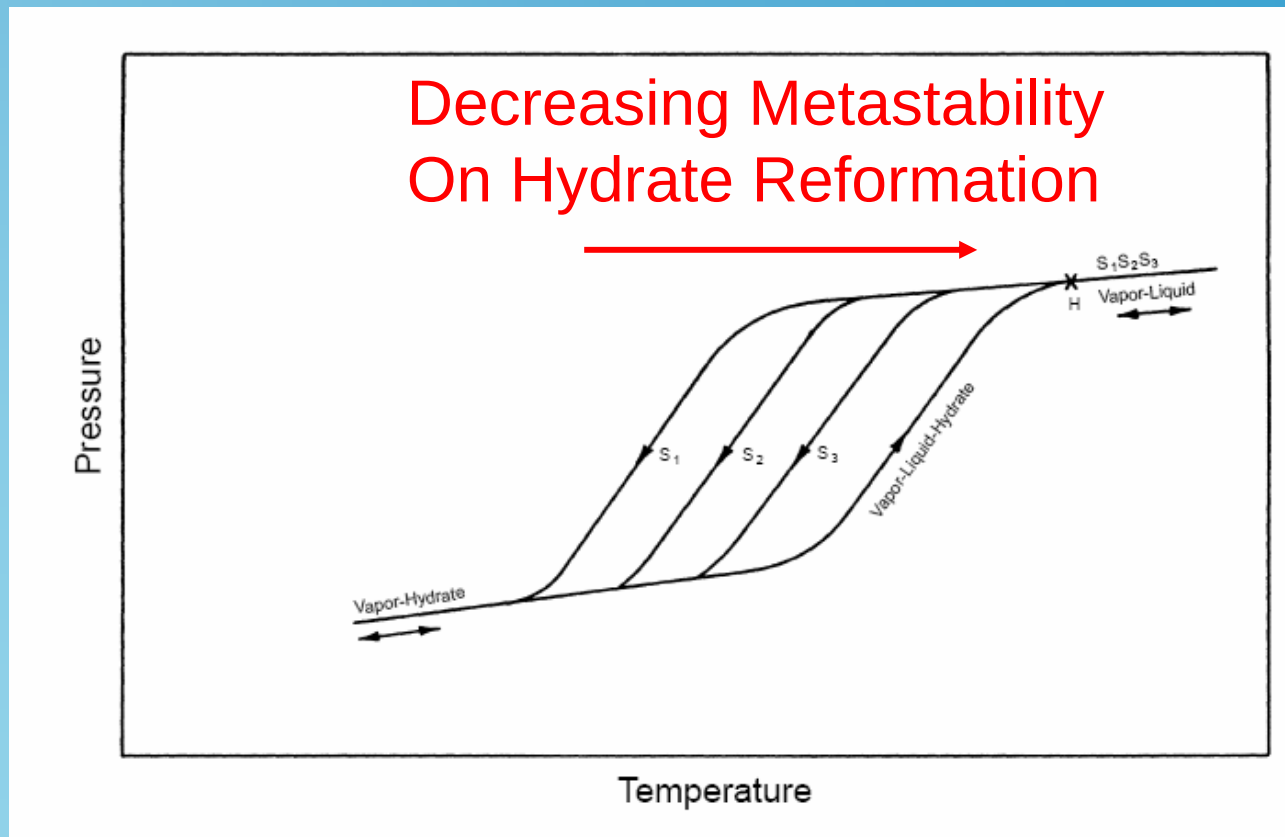


Investigating the well-documented 'memory effect phenomenon'

“Memory effect” causes more rapid nucleation

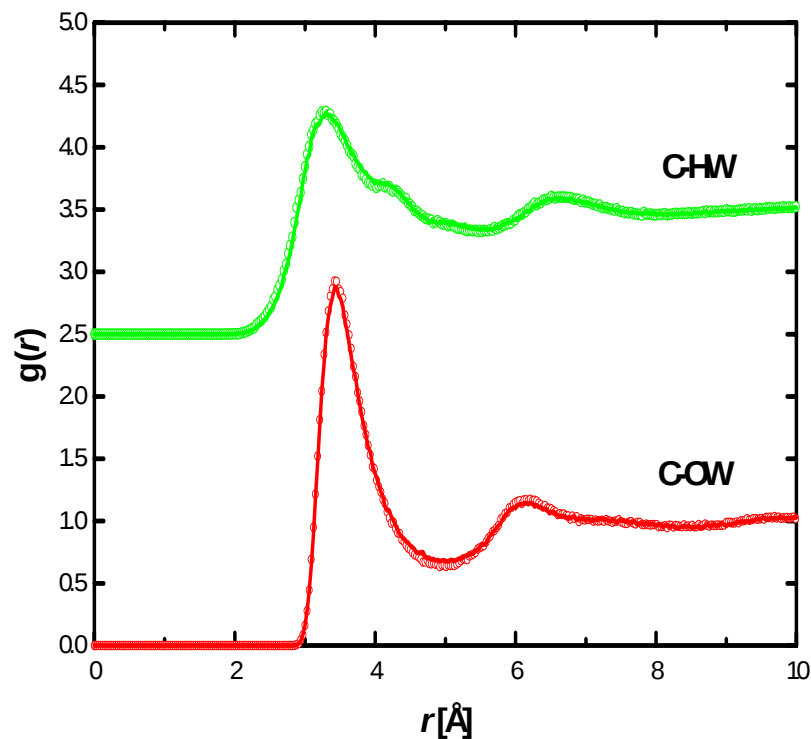
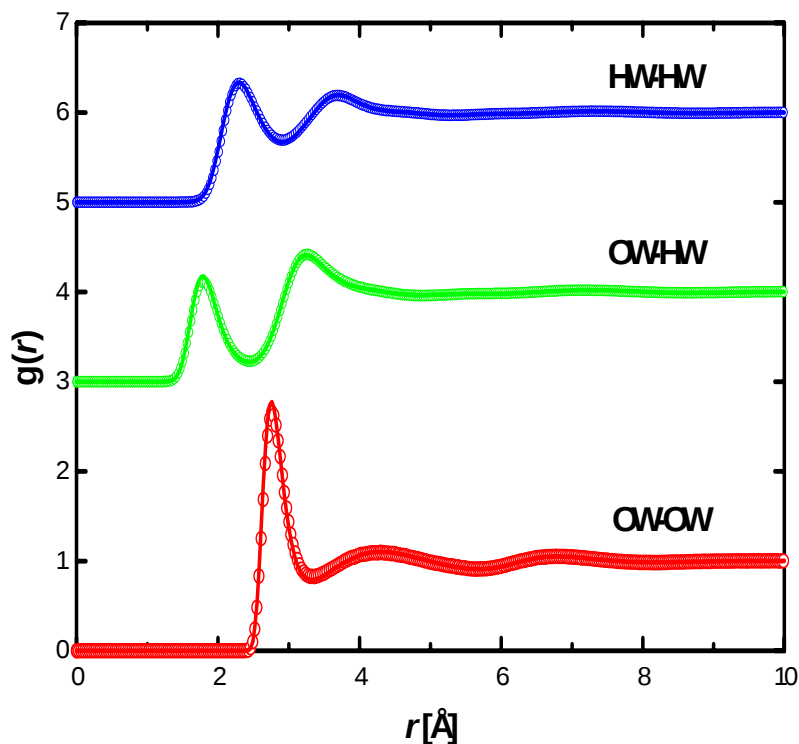
What causes the “memory effect”?

- Residual amorphous structure, residual crystallites, or dissolved gas



No Change in Water Structure & Hydration Shell Before Formation & After Melting

Before formation (points), after melting (solid lines)



'Residual' crystallites rather than amorphous structure attributed to the 'memory effect' phenomenon.



Future Directions: New Paradigms in Gas Hydrate Technology

Improve Understanding & Control of Kinetics in:

- Gas recovery from hydrate deposits
 - assess dissociation techniques
- Assessing submarine hydrate dissolution rates
 - impact of dissociation to the environment
- Energy storage materials
 - develop synthesis & stability technologies
- Maintaining flow in pipelines
 - determine when & where a plug occurs



Acknowledgements

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- National Undersea Research Program
- Minerals Management Services
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- DeepStar Consortium

Collaborators:

MBARI (P. Brewer, E. Peltzer)

LBNL (G. Moridas, T. Kneafsey)

RAL-ISIS, U.K. (A.K. Soper); ANL-IPNS (A.Schultz)

CVX (J.L. Creek); NTNU, Norway (J. Sjoblum); IFP, France (T. Palermo)

CSM (Matthew Liberatore, John Dorgan)

